DOI: 10.1002/ejic.200801141

Electro- and Photoinduced Formation and Transformation of Oxido-Bridged Multinuclear Mn Complexes

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Keywords: Manganese / Oxido ligands / Carboxylato ligand / Electrochemistry / Photochemistry

The extensive chemistry of oxido-bridged multinuclear manganese complexes arises to a large extent from their relevance to redox-active metalloenzymes such as manganese catalases and the oxygen-evolving complex of photosystem II containing, as active centres, oxido- and carboxylato-bridged dinuclear and tetranuclear Mn complexes, respectively. During the enzymatic catalytic cycles the oxidation state changes of the Mn ions induce some structural changes of these active centres such as the formation of oxido bridges. In this area, this review is focused on examples from the literature of the formation and transformation of oxido-bridged multinuclear manganese complexes that are induced by electrochemical or photochemical means. Representative examples of such transformations are provided by polypyridyl Mn complexes, with interconversion between mononuclear, dinuclear and tetranuclear cores accompanied by the concomitant formation or breaking of μ-oxido bridges. Other important examples are furnished by dinuclear Mn complexes having multipodal amino-pyridyl ligands, some of which contain phenolic units, for which a clean interconversion between μ-oxido and μ-acetato bridges are observed.

Introduction

The research interest in the chemistry of oxido-bridged multinuclear manganese complexes arises to a large extent from their relevance to biological systems such as manganese catalases (MnCat) and the oxygen-evolving complex (OEC) of photosystem II (PSII). (Note: Whereas in the cited articles "oxo" was used according to the former nomenclature rules, in this Microreview the new "oxido" nomenclature rules are applied.) These enzymes catalyze important biological redox reactions via oxido and carboxylato multinuclear manganese complexes as active centres. A dinuclear Mn complex is responsible for the disproportionation of H_2O_2 in MnCat, while the OEC of PSII, a cluster of four manganese and one Ca ions, catalyzes the light-driven water-oxidation reaction to generate dioxygen during

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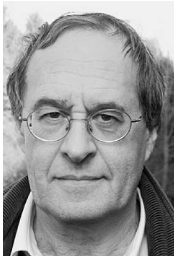
Marie-Noëlle Collomb was born in France in 1966. She received her Ph. D. from the Université Joseph Fourier (UJF) of Grenoble in 1993 under the supervision of Alain Deronzier, in the field of ruthenium carbonyl complexes and electrocatalytic carbon dioxide reduction. After a year of working with Prof. Marc Fontecave on alkanes oxidation catalysis as lecturer at UJF (1993–1994) she joined the Centre National de la Recherche Scientifique in 1994 as research scientist at UJF where she became Director of Research in 2007. She spent nine months in the groups of Professors Robert H. Crabtree and Gary W. Brudvig at Yale University (New Haven, USA) (1998–1999) as a CNRS research associate (NATO fellowship) on manganese chemistry. Her research interests deal with the synthesis, electrochemistry and photochemistry of metallic complexes (manganese, iron, and ruthenium) that mimic the active sites of redox metalloenzymes.



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photosynthesis. The oxidation state changes of the Mn ions during the enzymatic catalytic cycles (between II and IV) induce some structural changes of the active centres such as the formation of oxido bridges.

Since about 1980, hundreds of oxido-, alkoxido- and/or carboxylato-bridged manganese complexes comprising two to four metal ions have been synthesised that have provided models or at least some insight into the role of manganese in photosynthesis and several enzyme systems. Some of the core types that we will discuss in this review are shown in Figure 1. The ancillary ligands are N and/or O donors of various types (aliphatic, cyclic, polypyridyl and Schiff bases). These complexes have been obtained in the II–IV oxidation states with both homo and mixed valencies. Bridging oxido (O^{2-}) groups, which stabilise the high-valent oxidation state of Mn ions, are only present in complexes at the +III (d^4) and/or +IV (d^3) oxidation states. The majority of mixed valent complexes form crystallographically valence-trapped species with distinct sites for each oxidation level. The electronic (EPR), magnetic and electrochemical properties of these compounds have been extensively investigated and in some cases the catalytic properties for H_2O_2 disproportionation, H_2O oxidation or for reactions of other substrates have been evaluated. This extensive chemistry, covered in several recent reviews and special issues,[1–11] is not detailed here.

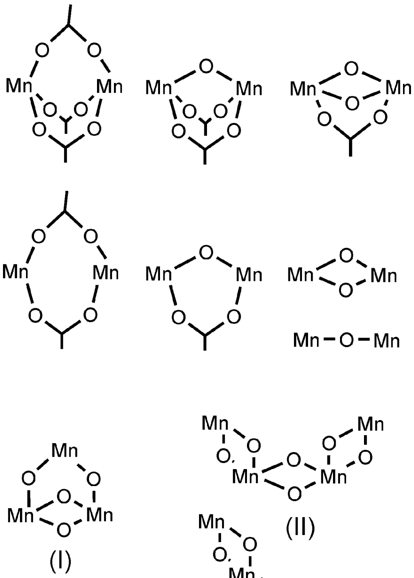


Figure 1. Examples of various types of manganese oxido, alkoxido, and/or carboxylato core structures.

Since the main objectives of this manganese chemistry is to mimic redox-active manganese metalloenzymes, a full understanding of the redox behaviour of these complexes is required, especially in order to design efficient functional models.

In this area, the aim of our review is focused on an aspect not developed in previous reviews and concerns the electro- and photoinduced formation or transformation of oxido-bridged multinuclear Mn complexes. Electrochemistry, commonly used to determine the redox potentials of transition metal complexes, is more rarely used to oxidize or reduce complexes in bulk in order to evaluate the stability of the electrogenerated species formed or to prepare new complexes. The review is therefore based on examples from the literature of manganese complexes for which an electron transfer is coupled to a chemical reaction inducing the formation of a new stable complex. The electrochemical oxidation or reduction can induce a change of the initial nuclearity of the complex (interconversion between mononuclear and dinuclear cores or between dinuclear and tetranuclear cores with the concomitant formation or breaking of oxido bridges). Another important type of electroinduced transformation observed is the interconversion of bridges in dinuclear manganese complexes between μ-acetato and μ-oxido, while the nuclearity of the complexes is not affected. In some of these studies the electron transfer is initiated photochemically, with the aim of modelling the photoinduced electron transfer in PSII.[12,13] The formation and transformation of oxido-bridged multinuclear Mn complexes are usually evidenced by coupling electrolysis and photolysis with analytical techniques such as UV/Vis and EPR spectroscopy.

Before presenting some representative examples of such electrochemistry and photochemistry, a short summary of the main information available relative to the MnCat and OEC systems is given.

1. Manganese Catalases and Photosystem II

It is now well established that the dinuclear manganese site present in MnCat can exist in at least four oxidation states, a reduced Mn_2^{II} form, a mixed-valent $Mn_2^{II,III}$ form, an oxidized Mn_2^{III} form and a superoxidized $Mn_2^{III,IV}$ form. However, there is no evidence to date for a Mn_2^{IV} state. This enzyme switches between the Mn_2^{II} and Mn_2^{III} forms during the catalysis, and only these two oxidation states are able to catalyze the disproportionation of H_2O_2 at extremely high rates; see Equations (1), (2), and (3).[1]

$$Mn_2^{II} + H_2O_2 + 2H^+ \rightarrow Mn_2^{III} + 2H_2O \tag{1}$$

$$Mn_2^{III} + H_2O_2 \rightarrow Mn_2^{II} + O_2 + 2H^+ \tag{2}$$

$$H_2O_2 \rightarrow 1/2O_2 + H_2O \tag{3}$$

Structural characterizations[14,15] of the oxidized Mn_2^{III} form reveal that the two metal centres are triply bridged by a $\mu_{1,3}$-bridging glutamate carboxylato and two oxygen atoms, (oxido and hydroxido). EXAFS studies suggest that the Mn–Mn separation is significantly longer in the reduced Mn_2^{II} form of the enzyme, so that both bridging oxygen atoms come from water and/or hydroxide.[1]

The oxidation of water is an energetically demanding reaction that requires the loss of four electrons and four protons and the formation of an O–O bond; see Equation (4).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E° = 1.23\text{ V vs. ENH (pH = 0)} \tag{4}$$

During photosynthesis dioxygen is evolved from the oxidation of water after the sequential absorption of four photons by the P_{680} chlorophylls in PSII.[2,12,13] At each step the excited state generated P_{680}^* becomes strongly reducing (the operating potential of P_{680}^+/P_{680}^* has recently been estimated to be close to –0.54 V vs. NHE)[16] and transfers one electron to a series of electron acceptors (a pheophytin D1 and two quinones, Q_A and Q_B). The resulting cation radical P_{680}^+, a powerful oxidant (P_{680}^+/P_{680}: $E \approx 1.25$ V)[16] oxidizes the manganese cluster via a tyrosine residue (Tyr_Z). The redox-active tyrosine is thought to also mediate the proton transfer coupled to the electron transfer. Oxygen evolution takes place after four consecutive oxidation steps of this type. These four steps are well summarized in the Kok cycle (Figure 2) where the five increasingly oxidized states of the Mn are denoted as S_0 to S_4.[17] It has been estimated that in all S-state transitions, the $Tyr_Z^{·+}/Tyr_Z$ potential for oxidation of the Mn complex is not significantly higher than 1.1 V.[18]

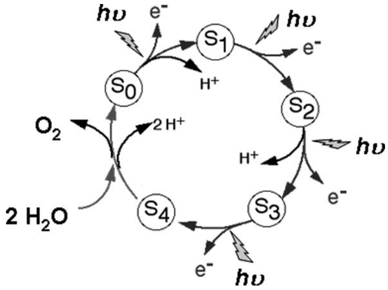


Figure 2. Kok cycle.

The exact structure of the OEC in PSII, an oxido-bridged Mn_4O_xCa cluster, as well as the detailed mechanism of water oxidation, remains unclear. On the basis of XAS and EPR spectroscopic data, it is generally accepted that the oxidation states in S_1 and S_2 are $Mn_2^{III}Mn_2^{IV}$ and $Mn^{III}Mn_3^{IV}$, respectively.[2,19] XAS studies have also provided evidence for the existence of Mn-(μ-O)$_2$-Mn (Mn–Mn distance of 2.7 Å) and Mn-(μ-O)-Mn (Mn–Mn distance of 3.3 Å) moieties in the cluster,[20] while the recent crystal structures of PSII[21–23] and subsequent polarized EXAFS measurements[24,25] have localised the Ca cation and suggest that the four Mn ions of the OEC are organized in a "3 + 1" fashion. From these structural data, it also appears that five or six carboxylato ligands from amino acid residues (aspartate, glutamate and alanine) are in positions such that they could act as bidentate ligands bridging different cations. Numerous mechanisms have been proposed for water oxidation.[9,18,26–28] For the formation of the O–O bond more recent mechanisms suggest a nucleophilic attack by water or hydroxide coordinated to either manganese or calcium, on an electrophilic Mn^V-oxido or Mn^{IV}-oxyl to form the O–O bond.

In both MnCat and PSII enzymes the oxidation state changes are accompanied by structural changes involving the groups bridging the Mn atoms. For example, in PSII it has been suggested that significant structural changes are coupled to the $S_0 \rightarrow S_1$ and the $S_2 \rightarrow S_3$ transitions[2,18,24,25] such as deprotonation of a μ-hydroxido bridge and the formation of an additional di-μ-oxido motif (oxidation of a five coordinate Mn^{III} to a six coordinate Mn^{IV} coupled to the formation of an additional μ-oxido bridge),[18] respectively. In addition, as suggested recently, the combination of bidentate carboxylato ligands and mono- or di-oxido bridges could enhance the stability of the cation arrangement and facilitate the rearrangement of the μ-oxido bridges during the S-state cycle.[23]

2. Polypyridyl Complexes (Bipyridine, Phenanthroline and Terpyridine)

The polypyridyl manganese derivatives are certainly the oldest studied manganese complexes in relation to the topic of this review. The pioneering work was performed by Sawyer and coworkers[29] using the bidentate 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) L ligands. They demonstrated that it is possible to electrochemically form oxido-bridged high-valent manganese complexes of the type $[Mn_2O_2(L)_4]^{3+/4+}$, from low-valent mononuclear $[Mn(L)_3]^{2+}$ complexes in CH_3CN.

2.1. Bidentate Ligands

The di-μ-oxido complexes $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ (L = bpy and phen) have been investigated in great detail as model compounds for the oxygen-evolving complex in photosystem II. The $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ and $[Mn_2^{III,IV/IV}O_2(phen)_4]^{3+/4+}$ complexes, isolated in the sixties,[30,31] were the first manganese complexes with oxido bridges to be synthesized. They were structurally characterized later[32–34] and their electrochemical, spectroscopic and magnetic properties were only published in 1977 by Cooper et al.[35,36] and Sawyer et al.[37] Electrochemical investigations were completed by our group ten years later, notably in aqueous solution.[38–42] EPR spectroscopic measurements of the mixed-valence complexes in CH_3CN at low temperature give an anisotropically broadened 16 line signal, centred at $g = 2.0$ with a hyperfine structure resulting from the two nonequivalent ^{55}Mn ($I = 5/2$) nuclei.[36] This signal has a strong resemblance to that of the multiline S_2 state signal of the PSII.[2] Their electrochemical behaviour in CH_3CN + 0.1 M Bu_4NClO_4 is characterised by a one-electron reversible oxidation located at 0.8–1.0 V vs. Ag/Ag$^+$ leading to the Mn_2^{IV} species, and a more or less reversible one-electron reduction (E_{pc} = –0.1–0.0 V), corresponding to the formation of the Mn_2^{III} species; see Equations (5) and (6). Table 1 summarizes the potential data for L = bpy, dmbpy (4,4′-dimethylbpy) and phen (see also ref.[43] for conversion of the potential vs. different reference electrodes).

$$[Mn_2^{III,IV}O_2(L)_4]^{3+} \rightleftarrows [Mn_2^{IV}O_2(L)_4]^{4+} + e^- \tag{5}$$

$$[Mn_2^{III,IV}O_2(L)_4]^{3+} + e^- \rightleftarrows [Mn_2^{III}O_2(L)_4]^{2+} \rightarrow [Mn^{II}(L)_3]^{2+} + \text{“}Mn^{IV}O_2\text{”} + L \tag{6}$$

The Mn_2^{III} species for all complexes are not stable on the time scale of bulk electrolysis. Subsequent chemically

Table 1. Cyclic voltammetry (CV) potentials of Mn polypyridyl complexes in CH_3CN at a scan rate of $100\ mV\,s^{-1}$ vs. Ag/Ag^+ (0.01 M $AgNO_3$ in CH_3CN + 0.1 M Bu_4NClO_4). Potentials referred to in this system can be converted into the ferrocene/ferrocenium couple by substracting 87 mV, or to SCE or NHE by adding 298 or 548 mV, respectively.

Complexes	$E_{1/2}$ [V] (ΔEp [mV])[a] $Mn_2^{III,IV}/Mn_2^{III}$	$Mn_2^{IV}/Mn_2^{III,IV}$	Ru^{III}/Ru^{II}	Ref.
$[Mn_2^{III,IV}O_2(phen)_4]^{3+}$	0.10 (65)	1.03 (65)		[37]
$[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$	0.04^{irrev}	1.02 (90)		[39]
$[Mn_2^{III,IV}O_2(dmbpy)_4]^{3+}$	–0.10^{irrev}	0.86 (80)		[39]
$[Mn_2^{III,IV}O_2\{Ru^{II}(bpy)_2(L^6)\}_4]^{11+}$	–0.12^{irrev}	0.82	0.90 (60)	[61]
$[Mn_2^{III,IV}O_2(terpy)_4(CF_3CO_2)_2]^+$	–0.08^{irrev}	0.74 (60)		[75]
		Mn^{III}/Mn^{II}	Ru^{III}/Ru^{II}	
$[Mn^{II}(phen)_3]^{2+}$		1.01 (250)		[29]
$[Mn^{II}(bpy)_3]^{2+}$		0.97 (180)		[29]
$[Mn^{II}(dmbpy)_3]^{2+}$		0.84 (470)		[29]
$[Ru^{II}(bpy)_3]^{2+}$			0.98 (80)	[39]
$[Mn^{II}\{Ru(bpy)_2(L^6)\}_3]^{8+}$		0.80^{irrev}	0.90 (70)	[62]
		Mn^{III}/Mn^{II}	Mn^{IV}/Mn^{III}	
$[Mn^{II}(terpy)_2]^{2+}$		0.96 (80)	1.77 (100)	[69]
$[Mn^{II}(p\text{Tol-terpy})_2]^{2+}$		0.91 (80)	1.63 (100)	[68]
$[Mn^{II}(t\text{Bu}_3\text{-terpy})_2]^{2+}$		0.85 (480)	1.56 (80)	[69]
$[Mn^{III}(terpy)(N_3)_3]$		–0.170 (100)	0.675 (70)	[77]

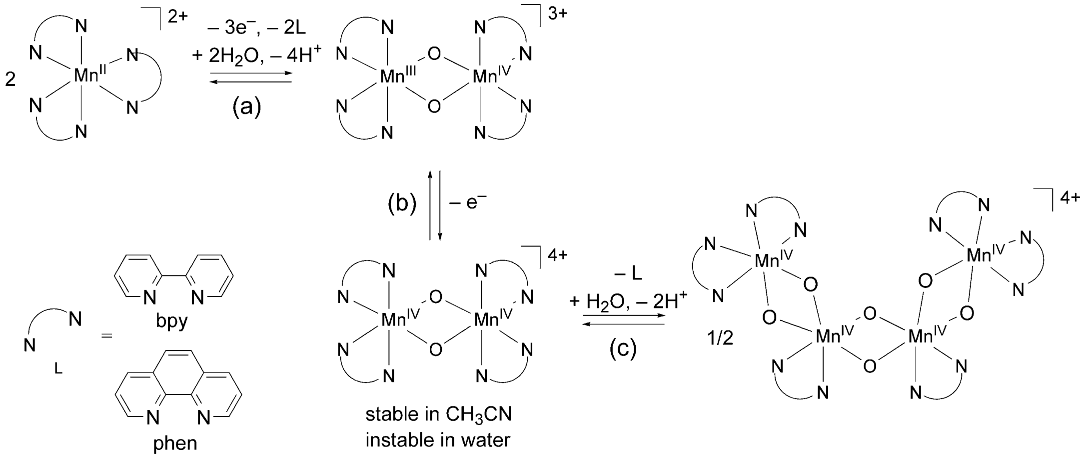
[a] $E_{1/2} = (Ep_a + Ep_c)/2$; $\Delta Ep = Ep_a - Ep_c$ (Ep_a = anodic peak potential; Ep_c = cathodic peak potential). Irrev: irreversible process, the potential given corresponds to the Ep value.

coupled reactions afford the mononuclear complexes $[Mn^{II}(L)_3]^{2+}$ associated with the formation of an undefined Mn^{IV} oxide species "MnO_2" and the release of L [Equation (6)].[38,39,41] In contrast, the $[Mn_2^{IV}O_2(L)_4]^{4+}$ species generated by oxidative electrolyses are perfectly stable for the dmbpy and phen derivatives, while some decomposition is observed for the bpy complex (the complex is formed in 75% yield).[35,37–39]

Cyclic voltammograms (CVs) of the corresponding mononuclear complex, $[Mn^{II}(L)_3]^{2+}$, in CH_3CN display three successive reversible ligand-centred reduction processes and a poorly reversible metal-based oxidation process, Mn^{III}/Mn^{II}, close to the oxidation potential of the corresponding di-μ-oxido dinuclear complex (Table 1).[29] However, the shape of the corresponding wave depends on the scan rate because of the chemical reaction coupled to the electron transfer.[39] A controlled potential oxidation of $[Mn^{II}(L)_3]^{2+}$ leads to the quasi-quantitative formation of the corresponding di-μ-oxido dinuclear complexes in their $Mn_2^{III,IV}$ or $Mn_2^{IV,IV}$ forms, depending on the potential applied; see Equation (7); Scheme 1, steps (a) and (b).

$$2[Mn^{II}(L)_3]^{2+} + 2H_2O \rightleftarrows [Mn_2^{III,IV}O_2(L)_4]^{3+} + 4H^+ + 2\,L + 3e^- \qquad (7)$$

The dimerization process is believed to be a result of the great instability of the $[Mn^{III}(L)_3]^{3+}$ species that disproportionates by reacting with residual water present in the solvent to form μ-oxido bridges via the release of one L ligand.[29] The formation of the oxido-bridged complexes in good yield from the deprotonation of water molecules is possible, owing to the concomitant release of free ligand L, which can act as a base to capture the proton that was



Scheme 1. Electrochemical interconversion for mono-, bi- and tetranuclear bpy and phen complexes in CH_3CN [steps (a) and (b)] and in an aqueous L/LH^+ buffered solution at pH 4.5 [for bpy: steps (a), (b) and (c), and for phen: steps (b) and (c)].

released.[29,38,39] The conversion of Mn^{II} into $Mn_2^{III,IV}$ [Equation (7)] is a fully reversible process; the initial Mn^{II} complexes are entirely reformed by a controlled-potential reduction of the electrogenerated $Mn_2^{III,IV}$ species at $E = -0.2$ V.

Similar electrochemical behaviour has been observed in aqueous solution for the bpy complex in a buffer of ligand ($bpy/bpyH^+$, pH range 4.3–5.4 + 0.1 M $NaBF_4$). Indeed, the $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ (L = bpy and phen) complexes are only stable in ligand buffered media.[35] The use of pure aqueous solutions or other buffers like acetate or phosphate causes very rapid decomposition of the complexes.[40–42,44,45] Previous electrochemical measurements have been performed in the absence of ligand buffers.[46,47] The Mn^{II}/Mn^{III} oxidation process of $[Mn(bpy)_3]^{2+}$ appears fully irreversible in water containing a buffer of ligand and is located at a lower potential than in CH_3CN [$Ep_a = 0.86$ V vs. Ag/AgCl (0.56 V vs. Ag/Ag^+), Table 2] because the coupled chemical reaction rate is faster in water. Carefully controlled potential oxidations of a solution of the complex at $E = 0.7$ V lead to the quantitative formation of $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ as in CH_3CN [Scheme 1, step (a)] [Equation (7)]. The shape of the CV of this $Mn_2^{III,IV}$ complex closely corresponds to that obtained in CH_3CN, with a quasi-reversible oxidation wave at $E_{1/2} = 1.16$ V vs. Ag/AgCl and an irreversible reduction wave at $Ep_c = 0.4$ V (Figure 3, A).[40,41] The main difference in behaviour compared with that in the CH_3CN medium arises from the poor stability of the electrogenerated Mn_2^{IV} species, which dimerizes after an exhaustive oxidation at $E = 1.25$ V to form the linear tetranuclear complex, $[Mn_4^{IV}O_6(bpy)_6]^{4+}$, quantitatively [Figure 1 core (II)] by the release of one bidentate ligand and the formation of two new oxido bridges; see Scheme 1, steps (b,c); Equation (8).

$$2[Mn_2^{III,IV}O_2(bpy)_4]^{3+} + 2H_2O \rightleftarrows [Mn_4^{IV}O_6(bpy)_6]^{4+} + 4H^+ + 2\,L + 2e^- \qquad (8)$$

The CV of $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ shows only an irreversible reduction peak close to that of $Mn_2^{III,IV}$ ($Ep_c = 0.40$ V) (Figure 3, B). These two electroinduced transformations [steps (a) and (b,c)] are quantitative. The whole transformation is also chemically reversible by reduction processes, although the two steps (b,c) and (a) are not clearly separated. Indeed, $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ cannot be generated quantitatively and selectively by reduction of $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ without any formation of $[Mn^{II}(bpy)_3]^{2+}$, since the reduction potentials of $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ and $[Mn_4^{IV}O_6(bpy)_6]^{6+}$ are too close.

In addition, it has been shown that the same electroinduced transformations can be achieved starting with the simple addition of Mn^{2+} cations to the $bpy/bpyH^+$ solution; the mononuclear $[Mn(bpy)_3]^{2+}$ complex is formed in-situ.

The tetranuclear complex $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ can be electrochemically prepared on a large scale and precipitated by addition of an excess of $NaBF_4$ to the oxidized solution.[41] After filtration the resulting brown powder exhibits the same characteristics as a previous sample prepared chemically by the disproportionation of $[Mn^{III}(bpy)Cl_3(H_2O)]$ in aqueous nitric acid solution[48,49] or by addition of K_2CrO_7 to a solution of dinuclear $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$.[50] It should be noted that $[Mn_4O_6(bpy)_6]^{4+}$ is EPR inactive at helium temperature owing to the S = 0 ground spin state while the one-electron reduced, mixed-valent $Mn_3^{IV}Mn^{III}$ form produced (transiently) by cryogenic radiolytic reduction of $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ exhibits a multiline EPR signal with a spectral width and intensity pattern comparable to that of the PSII S_2 state signal.[51] On the basis of our electrochemical investigations in water, a new synthesis of $[Mn_4^{IV}O_6(bpy)_6](BF_4)_4$ has been reported using $KMnO_4$ as the chemical oxidant.[41]

Table 2. Cyclic voltammetry potentials of Mn polypyridyl complexes in aqueous solutions at a scan rate of 20 mV s^{-1} vs. Ag/AgCl (3 M KCl in H_2O). Potentials referred to in this system can be converted to SCE by adding 20 mV.

Complexes		Ep_a [V] Mn^{III}/Mn^{II}	Ref.
$[Mn^{II}(bpy)_3]^{2+}$		0.86[a]	[40,41]
$[Mn^{II}(terpy)_2]^{2+}$		0.87[a]	[87]
	Ep_c [V] $Mn_2^{III,IV}/Mn_2^{III}$	$E_{1/2}$ [V] $Mn_2^{IV}/Mn_2^{III,IV}$	
$[Mn_2^{III,IV}O_2(phen)_4]^{3+}$	0.35	1.15	[42]
$[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$	0.40	1.16	[40,41]
$[Mn_2^{III,IV}O_2(terpy)_4(H_2O)_2]^{3+}$	0.53–0.64[b]	1.05	[87]
	Ep_c [V] $Mn_4^{IV} \rightarrow Mn_2^{III,IV}$		
$[Mn_4^{IV}O_6(phen)_6]^{6+}$	0.48		[42]
$[Mn_4^{IV}O_6(bpy)_6]^{6+}$	0.40		[40,41]
$[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$	0.82–0.91[b]		[87]

[a] Shoulder. [b] The Ep_c value depends on the supporting electrolyte.

For the phenanthroline derivatives,[42] while the tetranuclear complex can also be synthesized by such an electrochemical procedure, the poor solubility of mononuclear $[Mn(phen)_3]^{2+}$ in a $phen/phenH^+$ buffer prevents the electrosynthesis of the dinuclear complex; see Scheme 1, step (a).

This original electrochemical method for the selective preparation of high-valent polynuclear oxido-manganese complexes illustrates the great versability of electrochemistry for inorganic synthesis.

The electrochemical behaviours of the trinuclear $[Mn_3^{IV}O_4(L)_4(H_2O)_2]^{4+}$ (L = bpy and phen)[52,53] complexes having a triangular core [Figure 1, core (I)] have also been investigated.[41,42] In an aqueous L/LH^+ buffered solution these complexes present a reductive process as observed for $[Mn_4^{IV}O_6(L)_6]^{6+}$. Their reductions are slightly easier than $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ and $[Mn_4^{IV}O_6(L)_6]^{6+}$. As a consequence, by exhaustive reduction, $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ is formed with a maximum yield of 40%.

In some studies the mixed-valent dinuclear complexes $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ (L = bpy and phen) were associated with the generation of O_2 from water.[7,54–56] However, such complexes seem to be catalytically active only in heterogeneous systems; the dinuclear complex being electrochemically (immobilised on an electrode surface) or chemically

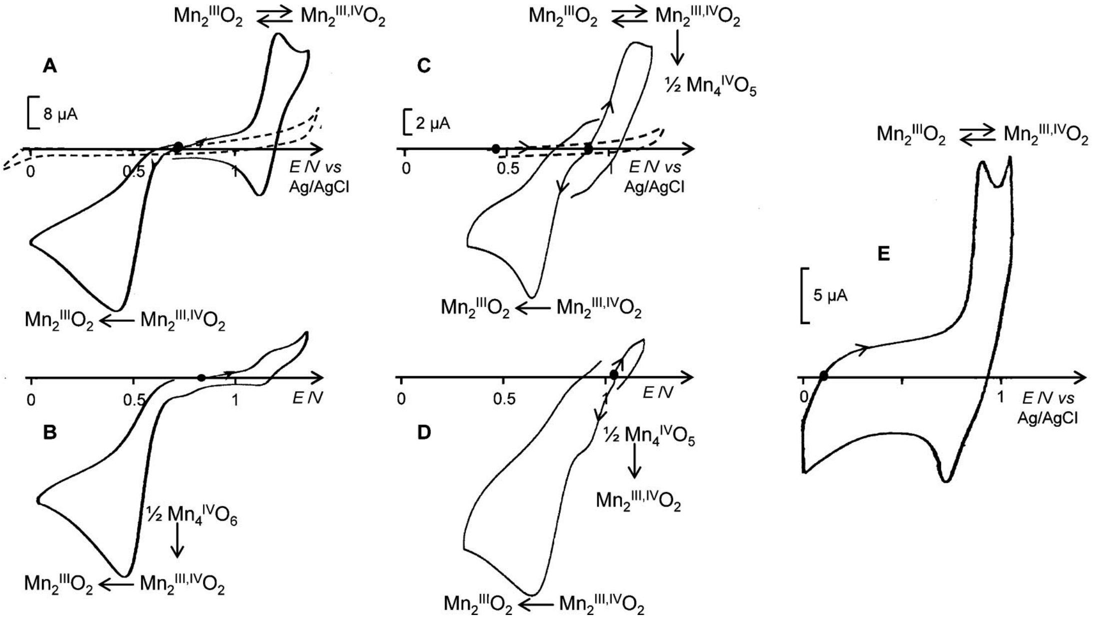


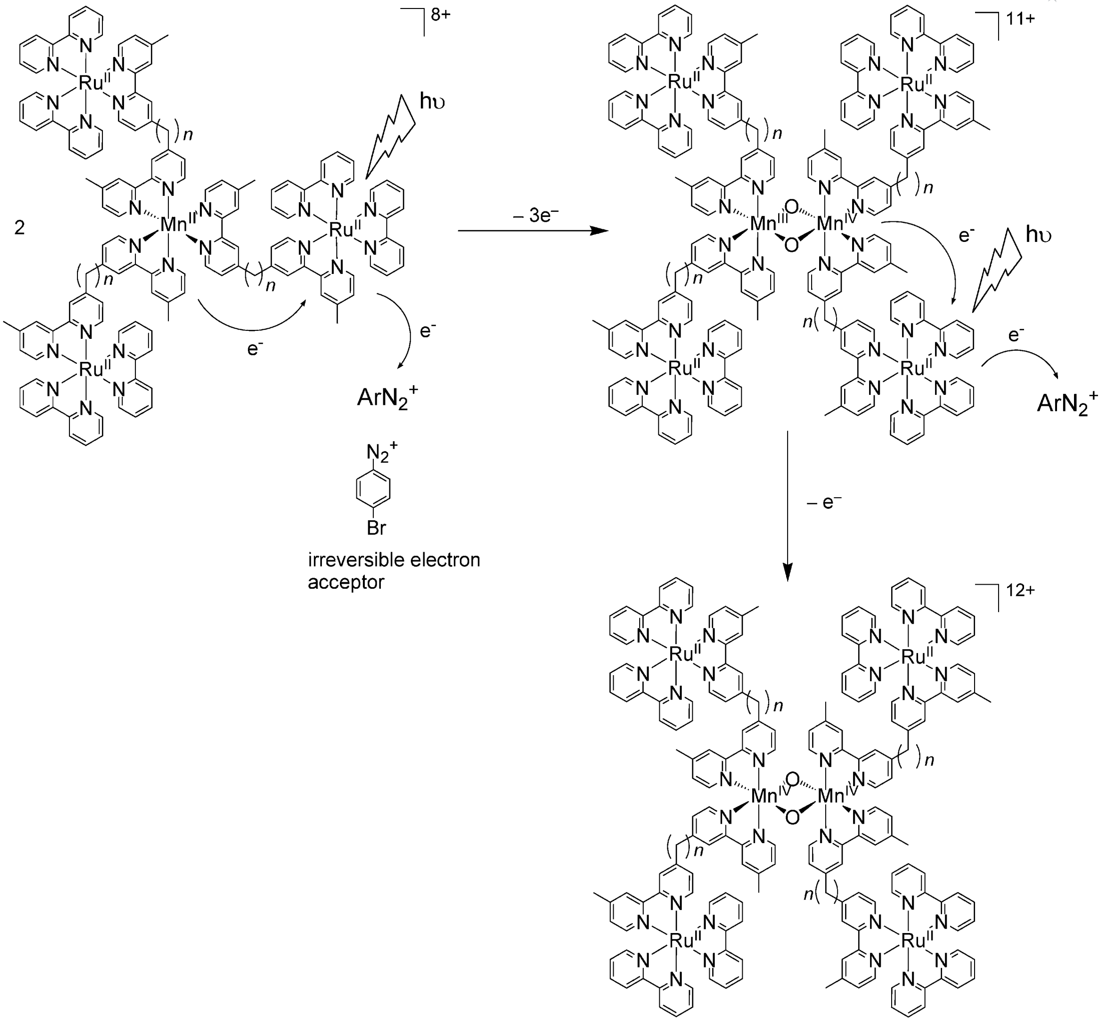
Figure 3. Cyclic voltammograms at a scan rate of 20 mV s^{-1} in aqueous solutions of: (A) a 2 mm solution of $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ at a vitreous carbon electrode (5 mm in diameter) in 0.05 m bpy/bpyH$^+$ buffer + 0.1 m $NaBF_4$ at pH 4.5 and (B) after exhaustive oxidation at 1.25 V {formation of $[Mn_4^{IV}O_6(bpy)_6]^{4+}$}. (C) A 2.6 mm solution of $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ at a vitreous carbon electrode (3 mm in diameter) in H_2O + 0.1 m KCF_3SO_3 at pH 4 and (D) after exhaustive electrolysis at 1.20 V {formation of $[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$}; (---) electrolytic solutions. (E) A carbon-poly$[Mn_2^{III,IV}O_2(L)_4]^{3+}$-modified electrode in H_2O + 0.1 m $LiClO_4$.

(with Ce^{IV}) oxidized. The assumed active species were $[Mn_2^{IV}O_2(L)_4]^{4+}$. However, these results have never been corroborated.[57] The instability of $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ in an aqueous solution, except in a L/LH$^+$ buffer, as well as the evolution of its one-electron oxidized form into a stable tetranuclear species makes the involvement of $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ as an active catalyst for water oxidation questionable.[40–42] Further evidence of the poor catalytic efficiency of these di-μ-oxido complexes even in heterogeneous media has been obtained from our studies conducted with thin films of polypyrroles functionalized by those compounds deposited on carbon electrode surfaces.[38,58,59] Such films have been elaborated following an indirect strategy implying the in-situ dimerization of the mononuclear complex previously immobilised in the film. The electroactivity of the resulting modified electrodes of $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ is characterized by the regular $Mn_2^{III,IV}/Mn_2^{IV}$ system of waves indicative of a perfectly reversible process (Figure 3, E) and no catalytic current is observed in aqueous solution.

In order to mimic the primary reaction steps on the donor side of PSII, we have evaluated the ability to photoinduce similar redox transformations of these polypyridyl manganese complexes. It has been demonstrated that di-μ-oxido complexes $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ (L = bpy and dmbpy) can be generated with high efficiency by photoinduced oxidation in CH_3CN of the corresponding mononuclear $[Mn^{II}(L)_3]^{2+}$ complexes using $[Ru^{II}(bpy)_3]^{2+}$ as a photosensitizer in the presence of an aryl diazonium salt, ArN_2^+, which acts as an irreversible electron acceptor.[39] The subsequent photooxidation leading to $[Mn_2^{IV}O_2(L)_4]^{4+}$ is efficient only in the case of the dmbpy complex, in agreement with the thermodynamic features of the reaction determined from electrochemical data. These oxidation processes involve the initial photoinduced generation of $[Ru^{III}(bpy)_3]^{3+}$ by reaction of the excited state of Ru^{II} with ArN_2^+, the latter being rapidly reversibly reduced in CH_3CN into ArH and N_2, thus preventing the back-electron transfer.[60] The following intermolecular electron transfer between $[Ru^{III}(bpy)_3]^{3+}$ and the Mn species is allowed only for $[Mn^{II}(L)_2]^{2+}$ and $[Mn_2^{III,IV}O_2(dmbpy)_4]^{3+}$ because their oxidation potentials are lower than that of the Ru^{III}/Ru^{II} couple. It is noteworthy that the efficiency of the second photoinduced oxidation is also quite high in spite of the strong quenching, presumably by an electronic energy transfer mechanism, of the ^{3}MLCT excited state of $[Ru^{II}(bpy)_3]^{2+}$ by $[Mn_2^{III,IV}O_2(dmbpy)_4]^{3+}$.

Extension of this work using a unimolecular polymetallic complex combining the properties of $[Ru^{II}(bpy)_3]^{2+}$ and $[Mn^{II}(L)_3]^{2+}$ moieties has also been achieved.[61,62] A better efficiency in terms of the kinetics of the electron transfer between the ground state $[Ru^{III}(bpy)_3]^{3+}$ and $[Mn^{II}(L)_3]^{2+}$ through an intramolecular process should be expected. Three heterotetranuclear complexes, $[\{Ru^{II}(bpy)_2(L^n)\}_3Mn^{II}]^{8+}$ have been synthesized and characterized, in which one Mn^{II}–tris(bipyridine) core is covalently linked to three Ru^{II}–tris(bipyridine)-like moieties via bridging bis(bipyridine) L^n ligands (Scheme 2).

In these compounds it appears that the irreversible oxidation of the Mn^{II} species into Mn^{III} ($Ep_a \approx 0.80$ V) associated with the formation of the $Mn_2^{III,IV}O_2$ core, as well as the oxidation of $Mn_2^{III,IV}O_2$ into $Mn_2^{IV,IV}O_2$ ($E_{1/2} \approx 0.80$ V) (Table 1), occurs at a less positive potential than that of the reversible oxidation of Ru^{II} moieties ($E_{1/2} \approx 0.90$ V). As a consequence, the three stable oxidized forms of the com-



Scheme 2. Schematic representation of the photoinduced electron transfers in tetra- and hexanuclear Ru-Mn complexes.

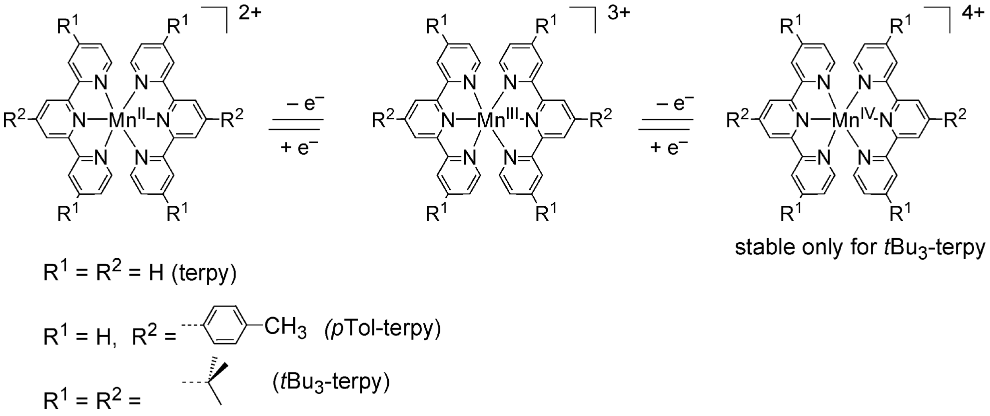
plexes, $[Mn_2^{III,IV}O_2\{Ru^{II}(bpy)_2(L^n)\}_4]^{11+}$, $[Mn_2^{IV}O_2\{Ru^{II}(bpy)_2(L^n)\}_4]^{12+}$ and $[Mn_2^{IV}O_2\{Ru^{III}(bpy)_2(L^n)\}_4]^{16+}$ have been sequentially obtained by electrochemical or photoinduced oxidation in fairly good yields. The efficiency of these transformations in CH_3CN is nearly quantitative in the presence of an extra base-like 2,6-dimethyl-pyridine (B). These experiments demonstrate that the electro- and photoinduced transformations of a tris(bipyridyl) Mn^{II} unit into the corresponding di-μ-oxido derivatives $Mn_2^{III,IV}$ can easily be accomplished even in a supermolecular structure in which the Mn moiety is surrounded by several Ru^{II}–tris(bipyridyl) units. The quantitative in-situ electrochemical formation of the di-μ-oxido complexes can also be achieved without the concomitant release of $[Ru^{II}(bpy)_2(L^n)]^{2+}$ in solution, starting from a simple mixture of $Mn(ClO_4)_2\cdot 6H_2O$, $[Ru^{II}(bpy)_2(L^n)]^{2+}$ and B in the respective ratio 1:2:2.[62]

The highly-charged hexanuclear complexes $[Mn_2^{III,IV}O_2\{Ru^{II}(bpy)_2(L^n)\}_4]^{11+}$ have been equally successfully prepared and isolated using *t*BuOOH[63] as the chemical oxidant in CH_3CN.[61]

2.1. Tridentate Ligands

Terpyridyl manganese complexes have been previously neglected in comparison with the bipyridyl and phenanthrolyl series. However, since it was reported in 1999[64] that the di-μ-oxido complex $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ is a water oxidation catalyst, this class of manganese complexes has attracted very strong interest.

The electrochemical behaviour of mononuclear bis(terpyridine) complexes $[Mn^{II}(L)_2]^{2+}$ {L = terpyridine (terpy) or substituted derivatives} remained unclear until very recently. A more or less reversible Mn^{II}/Mn^{III} system was observed in the CV[29,65–67] in CH_3CN (see Table 1 for potential values) but attempts at the characterization of the oxidized species formed by bulk electrolysis was unsuccessful.[29] We recently demonstrated that, in anhydrous CH_3CN, the Mn^{III} species resulting from oxidation of $[Mn^{II}(L)_2]^{2+}$ are markedly more stable than those using bipyridyl and phenanthrolyl derivatives.[68,69] Indeed, we succeeded in generating the $[Mn^{III}(L)_2]^{3+}$ species with L = terpy, *p*Tol-terpy and *t*Bu_3-terpy quantitatively by exhaustive electrolysis at E =



Scheme 3. Redox processes observed in Mn^{II}–bis(terpyridyl) complexes in anhydrous CH_3CN.

1.30 V and isolating and structurally characterizing the Mn^{III} *p*Tol-terpy derivative (Scheme 3), which is the first example of a mononuclear Mn^{III} polypyridyl complex.[68] The +III oxidation state of this complex was unambiguously established by a comparison with the X-ray data of the $[Mn^{II}(L)_2]^{2+}$ species.[67,70,71] We also showed that, in these strictly anhydrous conditions, in addition to the Mn^{II}/Mn^{III} process, a reversible redox process attributed to Mn^{III}/Mn^{IV} oxidation is observed in the CV at a higher positive potential (1.56–1.77 V, Table 1). Exhaustive electrolyses at E = 1.7–1.8 V have shown that the $[Mn^{IV}(L)_2]^{4+}$ species is only stable for L = tBu$_3$-terpy because of the presence of the three strong electron-donating *tert*-butyl groups on the ligand. This complex has been fully characterized in solution.[69]

Since $[Mn^{III}(L)_2]^{3+}$ species are more stable than the corresponding bidentate $[Mn^{III}(L)_3]^{3+}$ derivatives, the formation of multinuclear complexes with μ-oxido bridges requires a larger amount of H_2O in CH_3CN (≈2%). However, except for L = tBu$_3$-terpy, the corresponding mixed-valent dinuclear di-μ-oxido complexes cannot be obtained solely by electrochemical oxidation in this medium. A concurrent oxidation occurs producing a tetranuclear complex (see below) that is the final species resulting from the oxidative process.[72]

We recently synthesized a Mn–bis(terpyridyl) complex connected to two $Ru(bpy)_3^{2+}$-like units (Figure 4). Its CV in CH_3CN shows that the reversible Mn^{II}/Mn^{III} couple lies at an identical potential to those of the two Ru^{II}/Ru^{III} couples ($E_{1/2}$ = 0.92 V; ΔEp = 60 mV). Studies of its electrochemical and photoinduced oxidation are currently underway.[73] A previous example of a similar Ru-Mn molecule in which two moieties were covalently linked by an amide group has been reported; however, besides the reversible peak of the Ru^{II}/Ru^{III} couple, no electroactivity of the Mn moieties was detected.[74]

Another interesting electroinduced μ-oxido-bridge formation has been observed in CH_3CN containing a coordinating anion such as $CF_3CO_2^-$ as the supporting electrolyte (0.1 M). In this medium the oxidation of $[Mn^{II}(terpy)_2]^{2+}$ is fully irreversible (E_{pa} = 0.60 V) and an exhaustive oxidation at this potential furnishes $[Mn_2^{III,IV}O_2(terpy)_2(CF_3CO_2)_2]^+$ in nearly quantitative yield; see Equation (9).[75]

$$2[Mn^{II}(terpy)_2]^{2+} + 2H_2O + 2CF_3CO_2^- \rightleftarrows [Mn_2^{III,IV}O_2(terpy)_2(CF_3CO_2)_2]^+ + 2terpy + 2H^+ + 3e^- \qquad (9)$$

This μ-oxido $Mn_2^{III,IV}$ complex, also chemically prepared and crystallographically characterized, is reversibly oxidized to the stable Mn_2^{IV} species at a more positive potential ($E_{1/2}$ = 0.74 V, Table 1). In the same study the mono-μ-oxido compound $[Mn_2^{III}O(terpy)_2(CF_3CO_2)_4]$ was obtained during an attempt to crystallize the $Mn_2^{III,IV}O_2$ derivative. Unfortunately its redox properties were not evaluated since its dissolution in CH_3CN results in the formation of the corresponding $Mn_2^{III,IV}$ di-μ-oxido complex and a mononuclear Mn^{II} species. Electrochemical generation of $[Mn_2^{IV}O_2(terpy)_2(CF_3CO_2)_2]^{2+}$ has also been achieved starting from the azido $[Mn^{III}(terpy)(N_3)_3]$ complex.[76,77] This compound exhibits a quasi-reversible oxidation wave at 0.675 V (Table 1). However, an exhaustive electrolysis

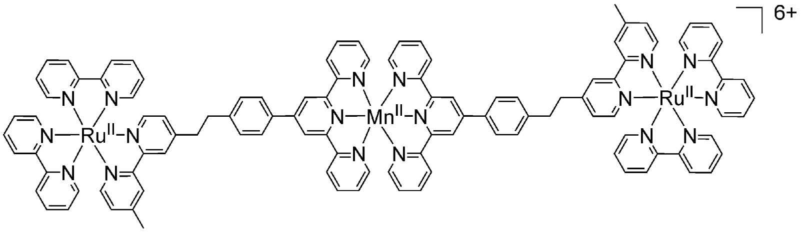


Figure 4. Schematic representation of the trinuclear Ru-Mn complex.

carried out in CH_3CN in the presence of 0.1 M $Et_4NCF_3CO_2$ at E = 0.8 V affords $[Mn_2^{IV}O_2(terpy)_2(CF_3CO_2)_2]^{2+}$ quantitatively. The one-electron oxidized $[Mn^{IV}(terpy)(N_3)_3]^+$ species reacts with residual water to give the di-μ-oxido complex while the N_3^- anions released during the oxidation are irreversibly oxidized to N_2; Equation (10).

$$[Mn^{III}(terpy)(N_3)_3] + H_2O + CF_3CO_2^- \rightarrow 1/2[Mn_2^{IV}O_2(terpy)_2(CF_3CO_2)_2]^{2+} + 2H^+ + 3N_3^- + e^- \quad (10)$$

When Bu_4NClO_4 is used instead of $Et_4NCF_3CO_2$ the oxidation of $[Mn^{III}(terpy)(N_3)_3]$ leads to an unidentified mononuclear Mn^{IV} complex.

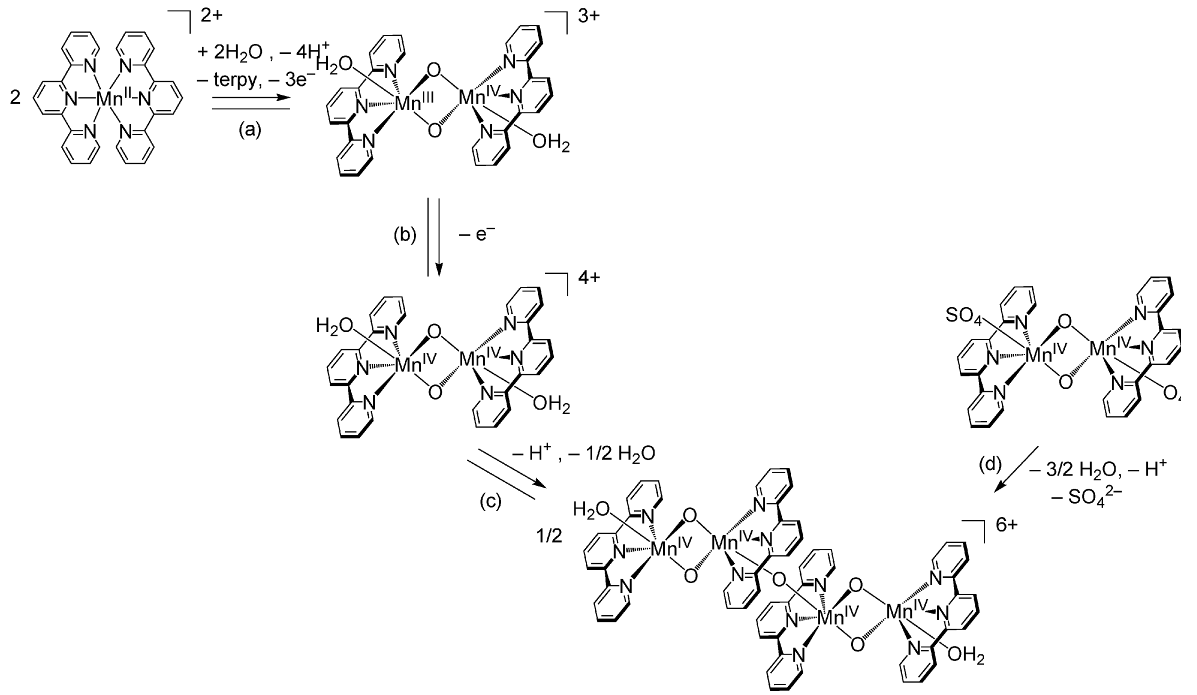
The synthesis of another di-μ-oxido complex with a terpyridyl ligand, namely $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$, has been reported independently by us[78] and the group of Brudvig and Crabtree.[64] In this complex each metal centre contains a terminal water molecule as in the dinuclear ruthenium complex, $[Ru_2^{III}O(bpy)_4(H_2O)_2]^{4+}$, which is known to act as an efficient molecular catalyst for water oxidation through the formation of the highly oxidized $[Ru^V{=}O]_2$ species.[79] Brudvig and Crabtree also reported that $[Mn_2^{III,IV}O(terpy)_2(H_2O)_2]^{3+}$ can catalyze water oxidation when oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) or sodium hypochlorite (NaOCl) is used as a primary oxidant.[64,80–82] This was the first di-μ-oxido complex considered as a structural model for the manganese complex in the OEC that could carry out catalytic O–O bond formation. However, the real source of oxygen atoms for O_2 evolution has been debated, since $KHSO_5$ and NaOCl are also oxygen-atom-transfer reagents.[2,57] Some attempts have also been reported using a pure electron-transfer oxidizing agent like Ce^{IV}. The observation of O_2 evolution in a homogeneous solution is still being discussed,[57,83,84] while when the complex is adsorbed into Kaolin clay the addition of a large excess of Ce^{IV} produces a significant amount of O_2.[57,85,86]

In order to have a better understanding of the real capability of this dinuclear complex to act as a catalyst for water oxidation we have investigated its electrochemical behaviour in aqueous solution as well as that of the corresponding mononuclear complex, $[Mn^{II}(terpy)_2]^{2+}$, in detail.[87] Since the electrode exchanges only electrons, if some O_2 evolution occurs, the source of oxygen atoms will undoubtedly be water. $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ is soluble and stable for several hours in aqueous solutions in the presence of terpyridyl buffer at pH 4 but also in unbuffered pure water at a pH of between 3 and 4.5. The electrochemical properties of $[Mn^{II}(terpy)_2]^{2+}$ and $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ have been investigated in these buffered and unbuffered aqueous solutions containing 0.1 M of different supporting electrolytes.[78,87] We found that the electrochemical behaviour of the terpy complexes in aqueous solution (Scheme 4) are basically the same as those of the bpy and phen complexes (Scheme 1). Indeed, electrochemical oxidation of $[Mn^{II}(terpy)_2]^{2+}$ at E = 0.85 V (Ep_a = 0.87 V, Table 2) allows the quantitative formation of $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ and, more importantly, the electrochemical oxidation of this latter complex at E = 1.20 V allows the quantitative build up of the stable tetranuclear Mn^{IV} complex, $[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$, having a linear mono-μ-oxido$\{Mn_2(\mu\text{-oxido})_2\}_2$ core [Figure 1 core (III)] (Scheme 4), which is stable for several hours in aqueous solution. The formation of this complex induces a decrease in pH of the solution from 4 to about 2.6, because of the release of protons involved in the formation of the new mono-μ-oxido bridge. The complex $[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$ was previously prepared chemically using oxone as the chemical oxidant and crystallographically characterized.[88]

If we compare the CV of $[Mn_2^{III,IV}O_2(L)_4]^{3+}$ (L = bpy and phen) and $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ (Figure 3, A and C) the main difference arises from the markedly lower stability of the corresponding $Mn_2^{IV}O_2$ species due to a more rapid evolution into a tetranuclear species. At the same scan rate the redox system $Mn_2^{III,IV}/Mn_2^{IV}$ appears much less reversible for the terpy complex than those of the bpy and phen congeners and lies at a less positive potential [$E_{1/2}$ = 1.05 V (terpy), 1.16 V (bpy) and 1.15 V (phen)] (Table 2).[40–42,87] These differences can be explained by a faster dimerization process following the one-electron oxidation process for the terpy complex.

Dimerization of $[Mn_2^{IV}O_2(L)_4]^{4+}$ (Scheme 1) requires the decoordination of one L ligand per dinuclear unit and the formation of two oxido bridges. In the case of the terpyridyl complex [Scheme 4, (c)] the aggregation of $[Mn_2^{IV}O_2(terpy)_2(H_2O)_2]^{4+}$ to form $[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$ does not require decoordination of a terpy ligand and involves the formation of only one oxido bridge between two dinuclear entities. In addition, the formation of this oxido bridge is facilitated because the $[Mn_2^{IV}O_2(terpy)_2(H_2O)_2]^{4+}$ species already contains aqua groups in its coordination sphere. Moreover, the easy reduction of $[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$ (Ep_c = 0.82–0.91 V) compared to $[Mn_4^{IV}O_6(L)_6]^{4+}$ {Ep_c = 0.40 V (bpy) and 0.48 V (phen)} (Table 2; Figure 3, B and D) is due, as well as in the case of their formation, to the difference in terms of kinetics of the coupled-electron-transfer chemical reactions. In contrast to the di-μ-oxido bpy and phen complexes, $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ is selectively and fully restored by an exhaustive reduction at E = 0.85 V as a consequence of the net separation of the reduction potentials of the di- (0.64 V) and tetranuclear (0.91 V) species. A further exhaustive reduction of $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ at E = 0.45 V reformed $[Mn^{II}(terpy)_2]^{2+}$ quantitatively.

The great tendency of the Mn^{IV} species to aggregate by the formation of oxido bridges is confirmed by the following experiment. Dissolution of the chemically prepared $[Mn_2^{IV}O_2(terpy)_2(SO_4)_2]$ complex,[80] in which SO_4^{2-} replaces the aqua ligands, in aqueous solutions leads to the quantitative formation of $[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$ after standing for a few hours. Moreover, $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ cannot act as an efficient homogeneous electrocatalyst for water oxidation since its one-electron oxidised product, $[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$, is stable in water. Although $[Mn_4^{IV}O_5(terpy)_4(H_2O)_2]^{6+}$ does not oxidize water, it is a remarkably powerful oxidant with a reduction poten-



Scheme 4. Electrochemical interconversion of mono-, bi-, and tetranuclear terpy complexes in an aqueous solution at pH 4.

tial of about 0.9 V vs. Ag/AgCl (0.92 vs. SCE). This potential is markedly higher than those of the other reported tetranuclear complexes for which the reduction potentials have been determined in aqueous solution: $[Mn_4^{IV}O_6(L)_6]^{4+}$ {Ep_c = 0.42 V (bpy) and 0.50 V (phen) vs. SCE, pH 4.5}[40–42] and $[Mn_4^{IV}O_6(bpea)_4]^{4+}$ (Ep_c = 0.18 V vs. SCE, pH 4).[89] Some preliminary experiments conducted in our group have shown that this tetranuclear species electrochemically catalyzes other oxidation reactions implying more simple processes, as for example the oxidation of alcohols.[87]

3. Multipodal Amino-Pyridyl Ligands

The chemistry of manganese with multipodal amino-pyridyl ligands is abundant and rich.[2] Most of the ligands utilized (tri- to hexadentate) are sufficiently flexible to allow coordination of all nitrogen atoms to one Mn centre, giving rise, in combination with oxido and carboxylato bridges, to a large variety of manganese complexes. Many of these have been tested as functional mimics of MnCat.[1]

3.1. Bis- and Tris(pyridyl)amine

One important feature of the series of complexes containing tri- and tetradentate N-donor ligands [two or three (2-pyridyl)alkyl arms attached to an aliphatic N atom, Figure 5] is that they allow the observation of a clean electrochemical interconversion of μ-acetato and μ-oxido bridges in dinuclear complexes.

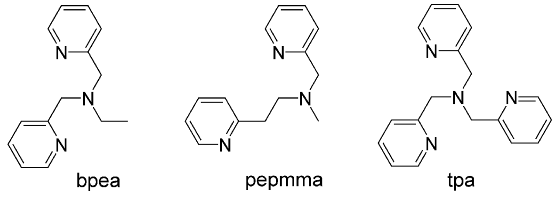


Figure 5. Schematic representation of the bis- and tris(pyridyl)-amine ligands.

3.1.1. Bis(pyridyl)amine

The synthesis and the basic electrochemical behaviour (CV) of the triply-bridged $[Mn_2^{III}O(O_2CCH_3)_2(L)_2]^{2+}$, $[Mn_2^{III,IV}O_2(O_2CCH_3)(L)_2]^{2+}$ and $[Mn_2^{IV}O_2(O_2CCH_3)(L)_2]^{3+}$ complexes was reported by Armstrong et al. for L = bpea[90–92] and Mukherjee et al.[93–95] for L = pepmma. These authors also showed the ability of these compounds to interconvert chemically by disproportionation reactions. For pepmma complexes it has also been demonstrated that this conversion can be accomplished by an electrochemical route.[95] Table 3 gives the potential of the different redox systems observed for these complexes, which depends on the scan rate used for the $[Mn_2^{III}O(O_2CCH_3)_2(L)_2]^{2+}$ complexes. While $[Mn_2^{III,IV}O_2(O_2CCH_3)(pepmma)_2]^{2+}$ is reversibly oxidised into $[Mn_2^{IV}O_2(O_2CCH_3)(pepmma)_2]^{3+}$ in CH_3CN ($E_{1/2}$ = 0.70 V vs. Ag/Ag^+), $[Mn_2^{III}O(O_2CCH_3)_2(pepmma)_2]^{2+}$ is irreversibly oxidised (Ep_a = 0.94 V) into $[Mn_2^{IV}O_2(O_2CCH_3)(pepmma)_2]^{3+}$ (Table 3). This latter complex has been generated by electrolysis. The oxidation process involves an electrochemical chemical electrochemical mechanism because of the instability of the one-elec-

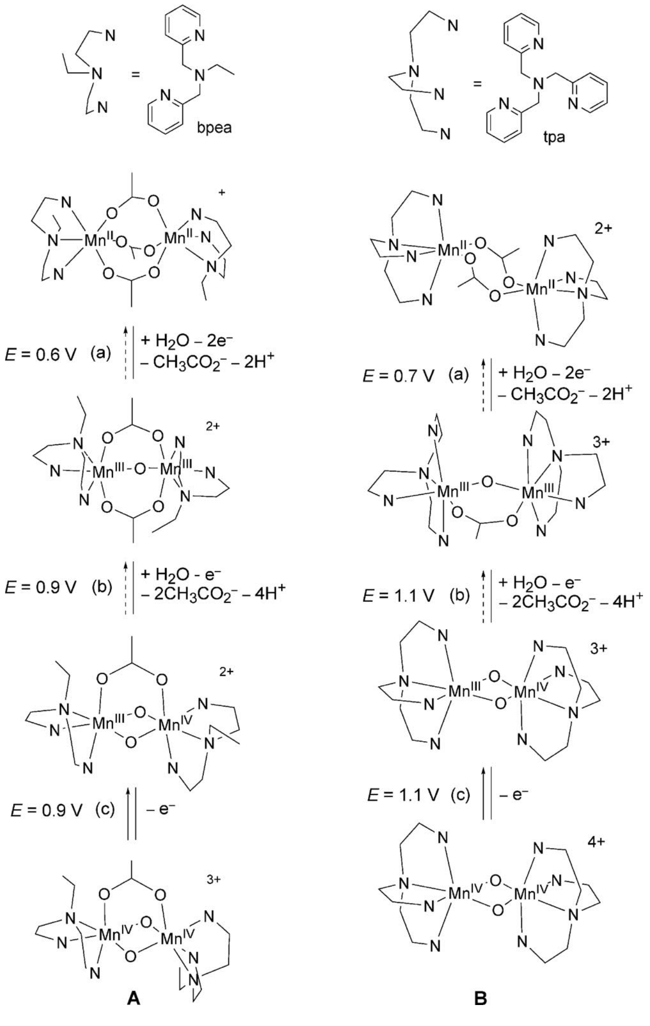
Table 3. Cyclic voltammetry potentials for dinuclear Mn complexes in CH_3CN at a scan rate of 100 mV s^{-1} vs. Ag/Ag$^+$ (0.01 M $AgNO_3$ in CH_3CN + 0.1 M Bu_4NClO_4). Potentials referred to in this system can be converted to SCE by adding 298 mV.

Complexes	Ep$_a$ [V] $Mn_2^{II,III}/Mn_2^{II}$			Ref.
$[Mn_2^{II}(O_2CCH_3)_3(bpea)_2]^{2+}$	0.44			[97]
$[Mn_2^{II}(O_2CCH_3)_3(tpa)_2]^{2+}$	0.70			[98]
	$E_{1/2}$ [V] $Mn_2^{III}/Mn_2^{III,II}$	$Mn_2^{III,IV}/Mn_2^{III}$	$Mn_2^{IV}/Mn_2^{III,IV}$	
$[Mn_2^{III}O(O_2CCH_3)_2(pepmma)_2]^{2+}$ [a]	-0.30^{irrev}	0.94^{irrev}, 0.90 at 1000 mV s^{-1}	–, –	[94,95]
$[Mn_2^{III}O(O_2CCH_3)_2(bpea)_2]^{2+}$[a]	-0.32^{irrev}, –0.35 at 500 mV s^{-1}	0.83^{irrev}, 0.76 at 500 mV s^{-1}	1.37 at 500 mV s^{-1}	[97]
$[Mn_2^{III}O(O_2CCH_3)(tpa)_2]^{3+}$	–0.07	0.95	1.45	[98]
		$Mn_2^{III,IV}/Mn_2^{III}$	$Mn_2^{IV}/Mn_2^{III,IV}$	
$[Mn_2^{III,IV}O_2(O_2CCH_3)(pepmma)_2]^{3+}$		-0.40^{irrev}	0.70	[93,95]
$[Mn_2^{III,IV}O_2(O_2CCH_3)(bpea)_2]^{3+}$		–0.29	0.61	[97]
$[Mn_2^{III,IV}O_2(tpa)_2]^{3+}$		–0.05	0.77	[98,104]
$[Mn_2^{III,IV}O_2(bpg)_2]^{+}$,		–0.34	0.43	[104]
$[Mn_2^{III,IV}O_2(pda)_2]$ in (CH_3CN/H_2O, 4:1)		-0.36^{irrev}	0.37	[104]

[a] The shape of the CV of the $[Mn_2^{III}O(O_2CCH_3)_2(L)_2]^{2+}$ complexes depends on the scan rate, and at a higher scan rate the waves appear more reversible. For $[Mn_2^{III}O(O_2CCH_3)_2(bpea)_2]^{2+}$ at 500 mV s^{-1}, in addition to the $Mn_2^{III}/Mn_2^{II,III}$ reduction and the $Mn_2^{III}/Mn_2^{III,IV}$ oxidation waves, the second oxidation process corresponding to $Mn_2^{III,IV}/Mn_2^{IV}$ has also been detected ($E_{1/2}$ = 1.37 V). Irrev: irreversible process, the potential given corresponds to the Ep value.

tron-oxidized form of the Mn_2^{III} complex, $[Mn_2^{III,IV}O(O_2CCH_3)_2(pepmma)_2]^{3+}$, which reacts with residual water in the solvent to form $[Mn_2^{III,IV}O_2(O_2CCH_3)(pepmma)_2]^{2+}$ by the substitution of an acetato bridge with an oxido bridge. Since $[Mn_2^{III,IV}O_2(O_2CCH_3)(pepmma)_2]^{2+}$ is more easily oxidizable than $[Mn_2^{III}O(O_2CCH_3)_2(pepmma)_2]^{2+}$, it is oxidized to $[Mn_2^{IV}O_2(O_2CCH_3)(pepmma)_2]^{3+}$ during the oxidation process.

These kinds of transformations were further developed by our group using bpea derivatives, including the corresponding tris(μ-acetato)dimanganese(II,II) complex.[96,97] It has been shown that the mono-μ-oxido $[Mn_2^{III}O(O_2CCH_3)_2(bpea)_2]^{2+}$ and bis(μ-oxido) $[Mn_2^{IV}O_2(O_2CCH_3)(bpea)_2]^{3+}$ complexes are selectively and nearly quantitatively generated by the successive exhaustive electrochemical oxidation of $[Mn_2^{II}(O_2CCH_3)_3(bpea)_2]^+$ in CH_3CN carried out at E = 0.6 V and 0.9 V (Scheme 5A). Indeed, the oxidation of $[Mn_2^{II}(O_2CCH_3)_3(bpea)_2]^+$ is fully irreversible (Ep$_a$ = 0.44 V) and leads to $[Mn_2^{III}O(O_2CCH_3)_2(bpea)_2]^{2+}$ {Scheme 5, step (a)}. This latter complex, as observed for the pepmma derivatives, is also irreversibly oxidized (Ep$_a$ = 0.83 V) to $[Mn_2^{IV}O_2(O_2CCH_3)(bpea)_2]^{3+}$ {Scheme 5, steps (b–c)}, which can be reversibly reduced to $[Mn_2^{III,IV}O_2(O_2CCH_3)(bpea)_2]^{2+}$ ($E_{1/2}$ = 0.61 V) (Table 3). It appears that each substitution of an acetato group by an oxido group is induced by a two-electron oxidation of the corresponding dimanganese complexes associated with deprotonation of water in the solvent. The protons released are probably in part trapped by the $CH_3CO_2^-$ released. Similar transformations have been observed if $[Mn_2^{II}(O_2CCH_3)_3(bpea)_2]^+$ is formed in situ either by the direct mixing of Mn^{2+} cations, the bpea ligand and CH_3COO^- anions with a 1:1:3 stoichiometry, or by mixing of the mononuclear complex $[Mn^{II}(bpea)_2]^{2+}$ and CH_3COO^- with a 1:1.5 stoichiometry.[97] Associated electrochemical back transformations were also investigated. It has been shown that these



Scheme 5. Electrochemical core interconversion of dinuclear bpea (A) and tpa (B) manganese complexes in CH_3CN. Electrolysis potentials vs. Ag/Ag$^+$ are indicated for the respective transitions.

transformations are chemically reversible by reduction processes, although the two steps are not separated. As a matter of fact, $[Mn_2^{II}(O_2CCH_3)_3(bpea)_2]^+$ is directly and fully regenerated by the reduction of $[Mn_2^{III,IV}O_2(O_2CCH_3)(bpea)_2]^{3+}$ preventing the selective regeneration of $[Mn_2^{III}O(O_2CCH_3)_2(bpea)_2]^{2+}$ since the reduction potentials of these complexes (Ep_c $Mn_2^{III,IV}/Mn_2^{III}$ = –0.4 V and Ep_c $Mn_2^{III}/Mn_2^{III,II}$ = –0.32 V, respectively) are too close (Table 3).

All these core interconversions under oxidative and reductive conditions are obviously concomitant with protonation/deprotonation reactions at the bridging oxido groups. It demonstrates that it is possible to chemically or electrochemically obtain dimanganese complexes containing the tridentate ligand bpea at various oxidation levels, (II,II), (III,III), (IV,IV) and its reduced (III,IV) form without dramatically modifying the overall structure of these dimers. The number of bridging oxido/acetato groups is directly correlated with the oxidation states of the manganese ion; increasing the number of oxido groups from zero to one and from one to two stabilizes the oxidation states of the manganese from (II,II) to (III,III) and (III,III) to (IV,IV) or (III,IV), respectively. A comparison of the catalase-like activity of all these bpea manganese complexes indicates than the Mn_2^{II} compound is far more active than the others.[97] The difference in activity vs. H_2O_2 disproportionation between the complexes has been attributed to differences in producing the active catalyst, which is thought to be a dihydroxidodimanganese(III) complex with the release of an acetato bridge.

3.1.2. *Tris(pyridyl)amine*

The same basic electrochemical behaviour is obtained with the bis(μ-acetato) complex $[Mn_2^{II}(O_2CCH_3)_2(tpa)_2]^{2+}$, which contains the tetradentate amino ligand tpa (Scheme 5, B), and only two acetato-bridging ligands instead of three.[98] The oxidation of $[Mn_2^{II}(O_2CCH_3)_2(tpa)_2]^{2+}$ in CH_3CN is also irreversible but occurs at a much more positive potential (Ep_a = 0.70 V) than for $[Mn_2^{II}(O_2CCH_3)_3(bpea)_2]^+$. Two successive controlled potential oxidations at E = 0.7 V and 1.1 V of a solution of $[Mn_2^{II}(O_2CCH_3)_2(tpa)_2]^{2+}$ allow the selective and nearly quantitative formation of the mono-μ-oxido mono-μ-acetato complex, $[Mn_2^{III}O(O_2CCH_3)(tpa)_2]^{3+}$ and the bis(μ-oxido) complex $[Mn_2^{IV}O_2(tpa)_2]^{4+}$, respectively. As for the bpea complexes, $[Mn_2^{II}(O_2CCH_3)_2(tpa)_2]^{2+}$ is directly and entirely regenerated by the reduction of $[Mn_2^{III,IV}O_2(tpa)_2]^{3+}$ or $[Mn_2^{IV}O_2(tpa)_2]^{4+}$. In contrast to $[Mn_2^{II}(O_2CCH_3)_2(tpa)_2]^{2+}$ and $[Mn_2^{III/III,IV}O_2(tpa)_2]^{3+/4+}$,[99–102] $[Mn_2^{III}O(O_2CCH_3)(tpa)_2]^{3+}$ has never been isolated using a conventional chemical method. This study allowed the electrochemical preparation and crystallographic characterization of this new dinuclear manganese complex in the tpa series. In addition, it has been shown that with the tpa ligand, the (III,III) oxidation state is stable with two types of cores, namely bis(μ-oxido) and mono-μ-oxido mono-μ-acetato. It should be mentioned that the three redox processes, $Mn_2^{III}/Mn_2^{II,III}$, $Mn_2^{III}/Mn_2^{III,IV}$ and $Mn_2^{III,IV}/Mn_2^{IV}$ observed in the CV of $[Mn_2^{III}O(O_2CCH_3)(tpa)_2]^{3+}$ appear to be more reversible than those observed for $[Mn_2^{III}O(O_2CCH_3)_2(bpea)_2]^{2+}$ at the same scan rate (Table 3). This shows that the rate of the chemical reaction leading to the formation of the bis(μ-oxido) complexes is slower in the case of the tpa complex.

From these electrochemical data it appears that the replacement of a $CH_3CO_2^-$ bridge by an oxido bridge induces a dramatic decrease (by more than 700 mV) of the potential of the $Mn_2^{III}/Mn_2^{III,IV}$ and $Mn_2^{III,IV}/Mn_2^{IV}$ redox couples (see Table 3 for bpea and tpa complexes).

The $[Mn_2^{III,IV}O_2(tpa)_2]^{3+}$ complex has quite good catalase-like activity.[103] However, in order to design more reliable manganese catalase models we decided to use the tripodal ligands in which carboxylate donors could easily be introduced and to investigate the reactivities of the corresponding complexes.[104] The ligands used in this study are depicted in Figure 6. These ligands involve successive replacements of pyridyl groups by carboxylate groups (see Table 3 for potential data). We found that the introduction of carboxylate groups leads to a large increase in the reaction rate of hydrogen peroxide disproportionation.

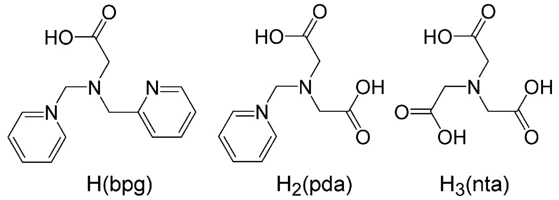


Figure 6. Schematic representation of the tripodal ligands with carboxylate donors.

This effect may probably be assigned to the ability of the carboxylate group to act as an internal base, since during the catalytic process hydrogen peroxide must be deprotonated and the protons transferred to oxido ligands to eliminate water molecules.

3.2. Substituted Ethane or Propanediamine Ligands

In a similar manner as found for polypyridyl derivatives, electrochemical formation of bridged-μ-oxido $Mn_2^{III,IV}$ complexes in CH_3CN can also be achieved by oxidation of mononuclear Mn^{II} species with these kinds of amine ligands. For instance, for Mn^{II} chlorido complexes containing the tetraamine ligands shown in Figure 7 (L^1 and L^2) the process requires the initial in-situ removal of the chlorido ligands by addition of Ag^+ [Scheme 6 (a)].[105]

In both cases exhaustive electrolysis carried out at E = 1.2 V and 1.4 V vs. SCE and in the presence of a base-like 2,6-lutidine (B), leads quantitatively to the di-μ-oxido $[Mn_2^{III,IV}O_2(L)_2]^{3+}$ complexes (see Table 4 for potential data). Remarkably, the dinuclear compound with L^2 has never been isolated using a conventional chemical method, in contrast to the L^1 complex. In this work the authors isolated crystals of the L^2 compound, and the X-ray structure reveals the *cis*-α conformation of L^2, in contrast to the

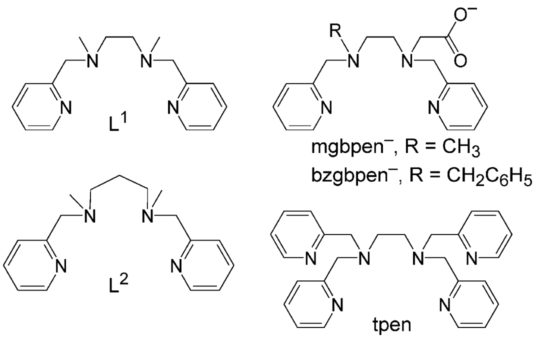
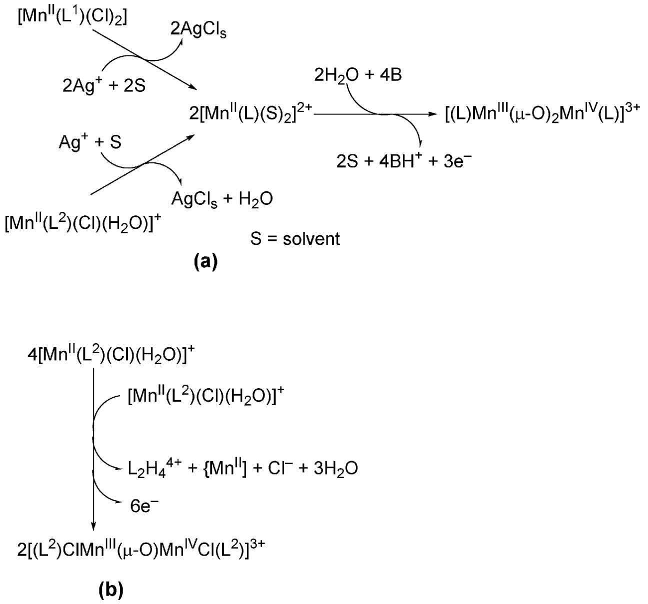


Figure 7. Schematic representation of substituted ethane or propanediamino-pyridyl ligands.



Scheme 6. Electrochemical formation of μ-oxido complexes from mononuclear chlorido complexes with L^1 and L^2 ligands, adapted from ref.[105]

more unusual *cis*-β conformation in the $[Mn(L^2)Cl(H_2O)]^+$ precursor. In the absence of base and without elimination of the exogeneous chloride ions the formation of the di-μ-oxido complex is prevented for the L^1 compound, the electrochemical oxidation leading quantitatively to $[Mn^{III}(L^1)(Cl)_2]^+$. For the L^2 compound the main oxidized species appears as the corresponding dinuclear mono-μ-oxido mixed-valent complex $[Mn_2^{III,IV}O(L^2)_2(Cl)_2]^{3+}$; see Scheme 6 (b). This difference of behaviour between the L^1 and L^2 complex is attributed to the more basic character of the ligand L^2.

By using L^1-like ligands in which one nitrogen is functionalized by a carboxylate group (Figure 7, ligands mgbpen⁻ and bzgbpen⁻) the formation of dinuclear oxido-bridged complexes has also been reported.[106] The chemical oxidation of $[Mn_2^{II}(L)_2(H_2O)_2]^{2+}$, in which two carboxylato ligands act as bridges between the two metal centres, by *t*BuOOH in CH_3CN leads to the di-μ-oxido Mn_2^{IV} complexes via the transient generation of mono-μ-oxido Mn_2^{III} species. Although these transformations have not been induced by electrochemical means, this system appears interesting as some oxygen evolution has been observed by oxidation of $[Mn_2^{II}(L)_2(H_2O)_2]^{2+}$ in water with Ce^{IV} or *t*BuOOH. However, experiments conducted with $H_2{}^{18}O$ are not sufficiently conclusive to indicate that the complex is a real catalyst for water oxidation.[107]

Table 4. Cyclic voltammetry potentials vs. SCE in CH_3CN for complexes with heptadentate L^1 and L^2 ligands.

Complex	$E_{1/2}$ [V] (ΔEp [mV]) Mn^{III}/Mn^{II}	 Mn^{IV}/Mn^{III}	Ref.
$[Mn^{II}(L^1)(Cl)_2]$	0.74 (70)	1.46 (75)	[105]
$[Mn^{II}(L^2)(Cl)(H_2O)]^+$	0.81 (90)	$1.65^{irrev[a]}$	[105]
	$Mn_2^{III,IV}/Mn_2^{III}$	$Mn_2^{IV}/Mn_2^{III,IV}$	
$[Mn_2^{III,IV}O_2(L^1)_2]^{3+}$	0.26 (100)	1.12 (105)	[105]
$[Mn_2^{III,IV}O_2(L^2)_2]^{3+}$	0.32 (70)	1.25 (95)	[105]

[a] Irrev: irreversible process, the potential given corresponds to the *E*p value.

Another example of the preparation of di-μ-oxido $Mn_2^{III,IV}$ complexes by bulk electrolysis has been reported, which involves the oxidation of two heptacoordinated Mn^{II} complexes of the tpen ligand (Figure 7), $[Mn^{II}(tpen)(H_2O)]^{2+}$ and $[(tpen)Mn^{II}(\mu\text{-}OAc)Mn^{II}(tpen)]^{3+}$.[108] In $[(tpen)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(tpen)]^{3+}$, the tpen ligand acts as a tetradentate ligand with two uncoordinated pyridylmethyl arms per ligand. With $[(tpen)Mn^{II}(\mu\text{-}OAc)Mn^{II}(tpen)]^{3+}$ another high-valent dinuclear complex is also obtained, $[(tpen)Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)Mn^{IV}]^{3+}$, and the ratio of the compounds is accurately controlled by the amount of added base.

4. Complexes with Amino Ligands Containing One or More Phenolic Units

Because of the bridging abilities of the phenolate oxygen atom towards metal ions, these kinds of ligands have been designed to coordinate two metal centres in close proximity to mimic the active site of metalloenzymes.[109] For Mn derivatives the initial objective was the elaboration of synthetic dinuclear complexes able to model the MnCat catalytic activity. It was subsequently found that the same complexes can also constitute good models for the PSII donor side. Most of these complexes also display interesting redox-induced transformations. However, because of the tendency of the phenolato ligands to be easily oxidized at the same time as the metal, these processes are often difficult to clearly identify.

4.1. Phenolic Ligands Bearing Two Side Arms

A large variety of these multidentate ligands (from penta- to heptadentate) have been successfully complexed by two manganese atoms, usually at the low oxidation states Mn_2^{II}, $Mn_2^{II,III}$ or Mn_2^{III} associated with two bridging carboxylato ligands.

4.1.1. Pentadentate Ligands

Most of the corresponding di-μ-carboxylato dinuclear manganese(II) complexes using symmetrical ligands of this type have been synthesised by Okawa et al. and studied as models of the active-site of MnCat.[110–114] Figure 8a shows the chemical structure of a typical complex of this series.

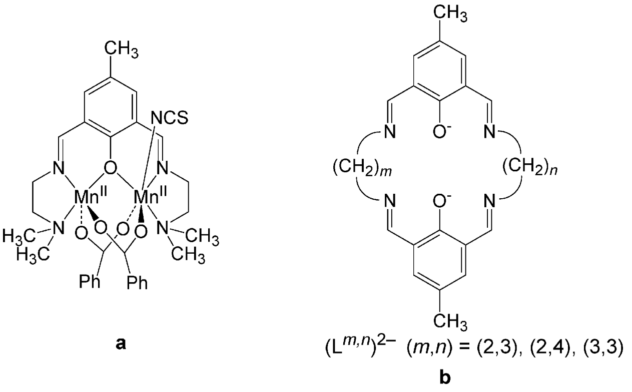


Figure 8. Schematic representation of (a) a di-μ-carboxylato dinuclear Mn_2^{II} complex with a pentadentate ligand and (b) macrocyclic hexadentate ligands containing two phenolate entities.

Cyclic voltammograms of these complexes at a scan rate of 400 mV s^{-1} in CH_2Cl_2 exhibit two or three quasi-reversible processes assigned to $Mn_2^{II}/Mn_2^{II,III}$, $Mn_2^{II,III}/Mn_2^{III}$ and $Mn_2^{III}/Mn_2^{III,IV}$ redox couples. However, by decreasing the scan rate the last process disappears, indicating the low stability of the Mn_2^{III} species. Although the formation of terminal oxido manganese(IV) species in catalase-like reactions using H_2O_2 in DMF solvent were reported, no electro-induced formation of μ-oxido manganese(IV) complexes has been confirmed.

4.1.2. Hexadentate Ligands

Di-μ-carboxylato-dimanganese complexes of such ligands are rare. One example involves a series of dinucleating macrocycles containing two phenolate entities (Figure 8, b). An electrochemical study of their Mn_2^{II} complexes indicated that for most of them the corresponding stable mixed-valent species $Mn_2^{II,III}$ could be obtained by electrolysis.[115,116] A more detailed electrochemical behaviour has been reported for complexes formed with the unsymmetrical hexadentate phenol-based ligand described in Figure 9 (a).[117]

The corresponding Mn_2^{II} and $Mn_2^{II,III}$ di-μ-dicarboxylato complexes have been synthesised and characterized. While the $Mn_2^{II}/Mn_2^{II,III}$ systems are fully reversible in CH_3CN and the two complexes can be quantitatively interconverted by electrolysis, the $Mn_2^{II,III}/Mn_2^{III}$ couple is only partially reversible. The instability of the Mn_2^{III} species has been confirmed by exhaustive electrolysis experiment, which consumes more than three electrons per molecule. The electrogenerated Mn_2^{III} species reacts, probably with residual water, leading to the formation of a μ-oxido Mn_2^{III} species that can further be oxidized to a higher valent di-μ-oxido species; the oxidation involves the removal of one carboxylate group as previously reported for other carboxylato Mn complexes (see above). This hypothesis has been confirmed by the preparation of the di-μ-oxido mono-μ-carboxylato $Mn_2^{III,IV}$ complex (Figure 9, b) by oxidation of the initial Mn_2^{II} complex with *tert*-butyl hydroperoxide (*t*BuOOH) in CH_3CN.[118] It should be noted that structural (X-ray absorption spectroscopy) and spectroscopic characterization have shown that in order to accommodate the formation of the Mn_2O_2 core the phenolic ligand changes its usual coordination mode. This complex, which is stable only at low temperature (–20 °C), exhibits the expected fully reversible $Mn_2^{III,IV}/Mn_2^{IV}$ redox couple in CH_3CN. Moreover, it has been demonstrated that, in contrast to the case of complexes involving pentadentate ligands,[110–114] oxidation by H_2O_2 in catalase-like reactions changes the initial structure of the complex by forming the mono and di-μ-oxido derivatives, which are the active species in the catalysis.[118,119]

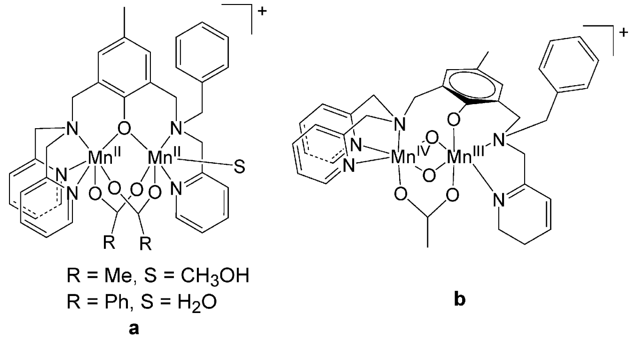


Figure 9. Schematic representation of (a) a di-μ-carboxylato dinuclear Mn_2^{II} complex and (b) the corresponding di-μ-oxido dinuclear $Mn_2^{III,IV}$ complex with a hexadentate ligand.

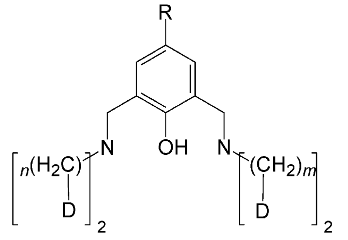
4.1.3. Heptadentate Ligands

In contrast to the above cases, numerous di-μ-carboxylato-dimanganese complexes containing heptadentate phenolate ligands have been prepared and described. Depending on the structure of the ligand, especially the presence of one or more phenolic units, the corresponding Mn_2^{II}, $Mn_2^{II,III}$ or Mn_2^{III} complexes are obtained.

N_6O Ligands

A series of N_6O ligands have been synthesised; most are symmetrical and their structures differ in the type of terminal amino arms (pyridyl, methylimidazolyl or triazanonyl; see Figure 10) attached to the aliphatic N atoms.[120–127]

For the bpmp ligand series both Mn_2^{II} and $Mn_2^{II,III}$ di-μ-carboxylato-dimanganese complexes have been isolated and characterized while for HL-Im and bcmp only the $Mn_2^{II,III}$ complex, and for LOH the Mn_2^{II} complex have been isolated. For all these compounds the CV displays the two expected $Mn_2^{II}/Mn_2^{II,III}$ and $Mn_2^{II,III}/Mn_2^{III}$ quasi-reversible systems with a large potential separation (>500 mV) in CH_3CN, indicating that the mixed-valent complexes are strongly stabilized (Table 5). However, electrolysis demonstrates that the Mn_2^{III} species are only partially stable.[124] In addition, studies of the series of bpmp complexes in



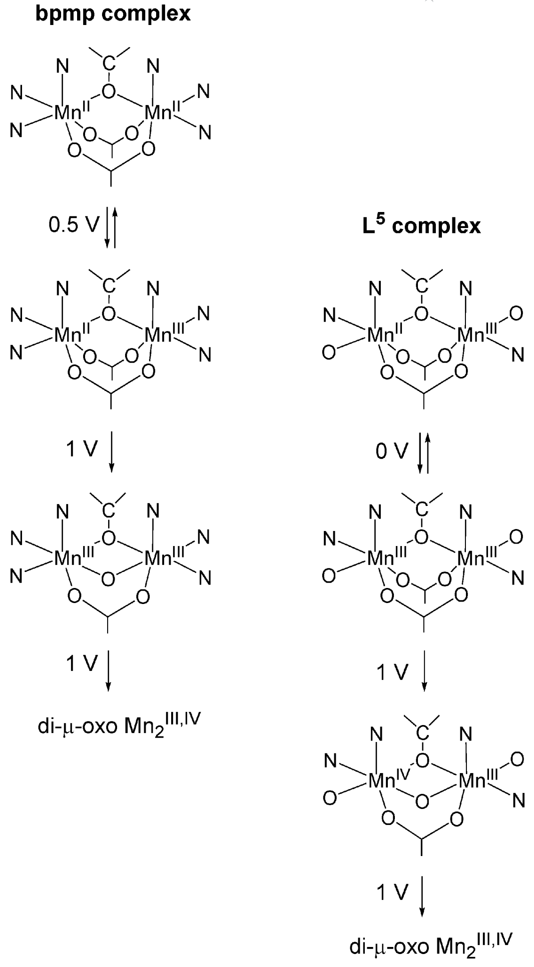
	R	n	m	D
LOH	H	2	2	2-pyridyl
bpmp	CH_3	1	1	2-pyridyl
bpmpa	CH_3	2	2	2-pyridyl
bpmpb	CH_3	1	2	2-pyridyl
HL-Im	CH_3	1	1	1-methylimidazol-2-yl
bcmp	CH_3	1	1	1,4,7-triazanon-1-yl

Figure 10. Schematic representation of the N_6O ligands.[120–127]

which the length of the chelate arms have been changed indicates that the increase of the length renders the $Mn_2^{II,III}/Mn_2^{III}$ redox system more irreversible.[126,127]

Recently the stabilities of the oxidized forms of the bpmp complex, $[Mn_2^{II}(bpmp)(OCCH_3)_2]^+$, have been investigated in detail by coupling electrolysis with a number of spectroscopic techniques (EPR, X-ray absorption, FT-IR and ESI-MS).[128,129] Scheme 7 (a) shows the suggested oxidation and accompanying structural changes occurring during the processes.

The observation of the different oxidized species as well as the mechanism of formation of the $Mn_2^{III,IV}$ species strongly depends on the water content of the CH_3CN solution. At 1% water content the first one-electron transfer proceeds without a bridge change while the second is coupled to the formation of an oxido bridge[129] accompanied by the loss of a carboxylato bridge, the final oxidation compound being the corresponding di-μ-oxido complex $Mn_2^{III,IV}$.[128] The ligand exchange reactions for the three one-electron steps occur in a potential range of 0.5 V.



Scheme 7. Scheme of suggested structural and oxidation state changes in di-μ-carboxylato dinuclear Mn complexes (a) with the bpmp ligand and (b) with the L^5 ligand. The approximative redox potentials of the respective transitions are indicated vs. SCE.

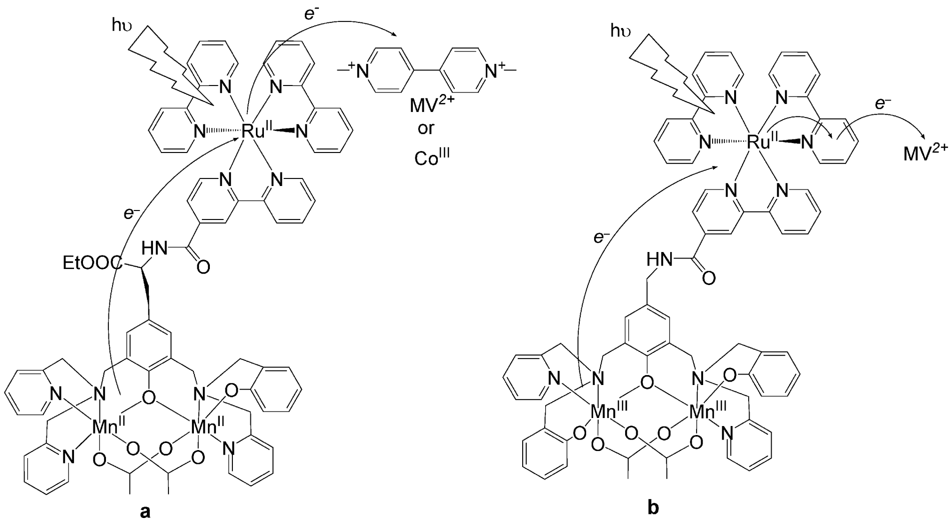
This bpmp Mn_2^{II} complex has been used for modelling the primary reaction steps on the donor side of PSII.[12,130–133] In this approach the oxidation of the dimanganese complex is photoinduced by a redox photosensitizer such as the $Ru(bpy)_3^{2+}$ complex, which plays the role of P_{680} chlorophyll pigments. Two different systems have been evaluated: a bimolecular one in which both complexes are simply mixed in solution and a monomolecular one where the dimanganese bpmp core is linked to $Ru(bpy)_3^{2+}$-like moieties. In this latter molecule, the phenolate group of the bpmp ligand plays the role of Tyr_Z in PSII (Scheme 8, a).

It has been reported that in both cases (inter- and intramolecular designs) and in the presence of an external elec-

Table 5. Cyclic voltammetry potentials vs. SCE in CH_3CN for dinuclear complexes containing a $Mn_2(\mu\text{-phenoxido})(\mu\text{-OCCH}_3)_2$ core with a heptadentate ligand.

Ligand	Complex	$E_{1/2}$ [V] $Mn_2^{II,III}/Mn_2^{II}$	$Mn_2^{III}/Mn_2^{II,III}$	$Mn_2^{III,IV}/Mn_2^{III}$	Ref.
N_6O	$[Mn_2^{II}(bpmp)(OCCH_3)_2]^+$	0.47	1.02	$1.75^{irrev[a]}$	[120,129]
	$[Mn_2^{II}(LOH)(OCCH_3)_2]^+$	0.79	1.30^{irrev}		[125]
	$[Mn_2^{II,III}(L\text{-}Im)(OCCH_3)_2]^{2+}$	0.455	1.03		[124]
	$[Mn_2^{II,III}(bcmp)(OCCH_3)_2]^{2+}$	0.27	0.75		[124]
		$Mn_2^{II,III}/Mn_2^{II}$	$Mn_2^{III}/Mn_2^{II,III}$	$Mn_2^{III,IV}/Mn_2^{III}$	
N_5O_2	$[Mn_2^{II,III}(L^3)(OCCH_3)_2]^+$	–0.23	+0.74	–	[137]
	$[Mn_2^{II,III}(L^4)(OCCH_3)_2]^+$	–0.21	+0.60	+0.97	[138]
N_4O_3	$[Mn_2^{III}(L^5)(OCCH_3)_2]^+$	–0.32	0.04	$0.96–1.13^{irrev}$	[139,140]

[a] Irrev: irreversible process, the potential given corresponds to the *E*p value.



Scheme 8. Schematic representation of a proposed pathway for the electron transfer following irradiation of some Ru-Mn_2 complexes in the presence of Co^{III} or MV^{2+}.

tron acceptor {methyl viologen (MV^{2+}) or $[Co^{III}(NH_3)_5Cl]^{2+}$ (Co^{III})} the manganese complex is photo-oxidised in a similar fashion through the transient photogenerated Ru^{III} species in three subsequent steps to give the $Mn_2^{III,IV}$ species (Scheme 8, a). The primary electron transfer between the generated Ru^{III} species and the Mn_2^{II} centre to form the $Mn_2^{II,III}$ species occurs following an intramolecular process ($k_{ET} > 10^7$ s^{-1}) in the monomolecular system. This behaviour has been essentially evidenced by repeated flash photolysis coupled with EPR spectroscopic experiments.[130–133] Although no water oxidation was detected with this system,[84,132] it was the first reported example of a light-driven multiple oxidation of a manganese complex.

Finally, it should be noted that the bpmp dimanganese di-μ-carboxylato core can also act as an efficient electron donor in a donor-chromophore-acceptor triad architecture in which $Ru(bpy)_3^{3+}$ is the photosensitizer and two naphthalene diimine moieties are acceptors (Figure 11).[134] An unusually long-lived photoinduced charge separation of 600 μs at room temperature has been observed, reaching 0.1–1 s at 140 K. This slow charge recombination can be explained by an unusually large reorganization energy resulting from the inner reorganization of the dimanganese complex.

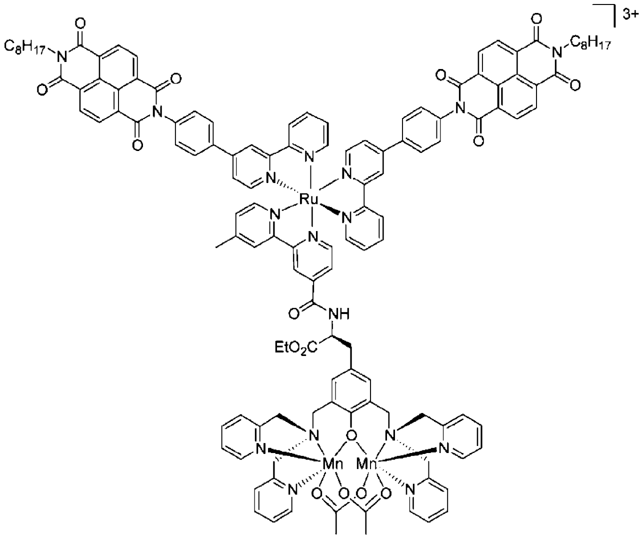


Figure 11. Schematic representation of the structure of the Mn_2-containing triad. (Figure reproduced from ref.[134], with permission from AAAS).

N_5O_2 and N_4O_3 Ligands

In order to try to improve the capabilities of these kinds of dimanganese complexes to reach higher valent manganese species, similar ligands to that of bpmp but containing a larger O/N ratio have been synthesised by replacing one or two amino groups with phenols (N_5O_2 and N_4O_3 ligands). These ligands were synthesised following a similar synthetic approach previously described for Fe_2^{II} complexes,[135,136] and their respective corresponding $Mn_2^{II,III}$ and Mn_2^{III} dimanganese di-μ-carboxylato complexes have been prepared.[137–139] Figure 12 gives an example of both kinds of complexes.

For the N_4O_3 complex, $[Mn_2^{III}(L^5)(OCCH_3)_2]^+$, the higher number of oxygen donors greatly stabilizes the Mn_2^{III} form, so the potentials of the $Mn_2^{II,III}/Mn_2^{III}$ and $Mn_2^{II}/Mn_2^{II,III}$ redox couples are dramatically lowered compared to the similar couples for the bpmp complex, as determined by cyclic voltammetry (see Table 5 for a comparison of the potentials data).[139] This complex is oxidized in two very close poorly reversible one-electron steps indicating that the oxidation process is complicated in CH_3CN. However, it has been shown by EPR and absorption spectroscopic analysis that if a large amount of a $Mn_2^{III,IV}$ oxido species is formed, further oxidations probably involve the phenolate moiety. The formation of one or two μ-oxido bridges associated with the release of one or two carboxylato bridges occurs only when the complex is oxidized at the $Mn_2^{III,IV}$ level (Scheme 7, b). The presence of water in CH_3CN is also required to efficiently perform this electro-

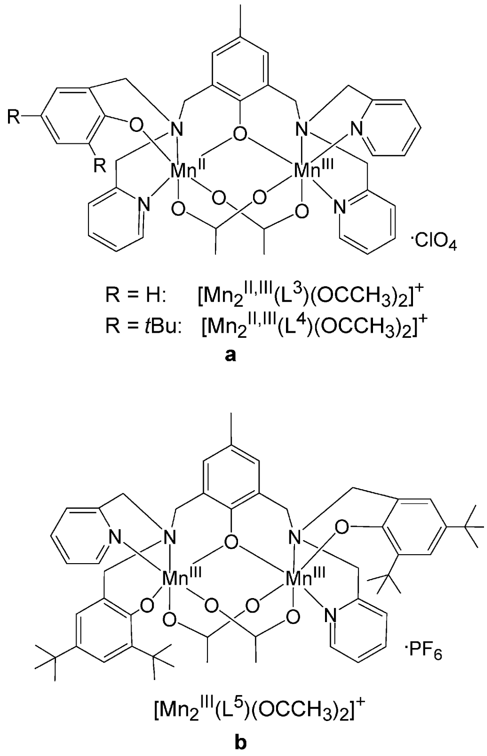


Figure 12. Schematic representation of bis(carboxylato)-dimanganese complexes with (a) N_5O_2 and (b) N_4O_3 ligands.[139]

or photoinduced [by $Ru(bpy)_3^{2+}$] transformation. In contrast, the electrogenerated Mn_2^{II} species is less stable and moves partly into an unidentified paramagnetic species resulting presumably from a large ligand environmental change rather than loss or exchange of ligands.[139,140]

A similar behaviour is observed for the di-μ-carboxylato $Mn_2^{II,III}$ complexes containing N_5O_2 ligands (Figure 12, a). As expected this N_5O_2 core also stabilizes the higher oxidized states but to a lower extent. These complexes exhibit the quasi-reversible one-electron oxidation and reduction waves of the $Mn_2^{II}/Mn_2^{II,III}$ and $Mn_2^{II,III}/Mn_2^{III}$ redox systems in their CV, while a second oxidation wave is also seen, which becomes quasi-reversible at high scan rates ($100\ V\,s^{-1}$). In anhydrous CH_3CN the final oxidized species have not been clearly identified while, as for other phenolato-bridged complexes, addition of water favours the formation of μ-oxido species. However, it has been shown that at high water concentrations ligand exchange occurs in the Mn_2^{III} and also in the $Mn_2^{II,III}$ species,[132] where a carboxylato bridge is replaced by two terminal aqua ligands. Moreover, a complex containing the N_4O_3 ligand without the di-*tert*-butyl substituents, connected to a $Ru(bpy)_3^{3+}$centre (Scheme 8, b) has also been prepared and studied.[141] A slightly higher intramolecular electron-transfer rate constant ($k_{ET} > 5 \times 10^7\ s^{-1}$) has been observed for the reaction between the photogenerated $Ru^{III}(bpy)_3^{3+}$ site and the dimanganese centre than that for the bimolecular complex containing the bpmp core in Scheme 8 (a).

N_2O_5 Ligands

Examples of complexes with this kind of ligand are very rare. The most representative is a bpmp-like ligand in which the four pyridyl arms are replaced by four methoxyl arms. The resulting Mn_2^{II} di-μ-carboxylato derivatives are much more difficult to oxidize than the other bpmp related complexes by around 0.5 V. Moreover, the oxidation process becomes irreversible, with the one-electron oxidation $Mn_2^{II,III}$ species undergoing a fast unidentified subsequent chemical reaction.[142]

4.2. Phenolic Ligands Bearing One Side Arm

Mn complexes containing pentadentate phenolate ligands will be considered here. Metallation of these ligands by manganese(II) preferentially gives dinuclear complexes in which two phenolate ligands act as bridges between the two metal centres. In some cases mononuclear manganese complexes have also been isolated.

N_4O Ligands

A series of ligands of this type has been synthesised (structures given in Figure 13), which differ in the relative position of the phenol group and the presence or absence of an imine group. Reaction of $L^{a\prime}H$ with $Mn^{III}(O_2CCH_3)_2\cdot 2H_2O$ affords a dinuclear Mn_2^{III} complex bridged by a single unsupported oxido group. However, during the complex synthesis spontaneous dehydrogenation of the ligand occurs and the final complex appears as the dinuclear complex $[Mn_2^{III}O(L^{i\prime})_2]^{2+}$.[143] The CV of this complex shows two successive reversible one-electron anodic waves in CH_3CN (Table 6). The stable one-electron oxidized form $[Mn_2^{III,IV}O(L^{i\prime})_2]^{3+}$, obtained by exhaustive electrolysis, has been structurally characterized. This oxidation has also been observed by reaction with a tyrosyl radical generated by electron transfer through a photogenerated $Ru(bpy)_2^{3+}$ species[144] in a similar fashion to that described above. The second reversible one-electron process occurring at a 0.45 V more positive potential than the first is attributed to the formation of a $[Mn_2^{IV}O(L^{i\prime})_2]^{4+}$ species in which one phenolate group of the ligand is oxidized rather than the oxidation of $Mn_2^{III,IV}$ to Mn_2^{IV}. Indeed, the formation of a phenoxyl radical was evidenced by low-temperature resonance Raman spectroscopy experiments. A dinuclear Mn_2^{II} phenolato-bridged complex, $[(L^{i\prime})Mn^{II}Mn^{II}(L^{i\prime})]^{2+}$, has also been synthesised using the $L^{i\prime}$ ligand.[145] This complex can withstand a two-electron electrochemical oxidation in CH_3CN leading to the Mn_2^{III} forms, which maintain the phenolate groups as bridging ligands (Scheme 9).

Upon air oxidation of the Mn_2^{II} complex, the mono-μ-oxido $[Mn_2^{III}O(L^{i\prime})_2]^{2+}$ is obtained, while the corresponding mixed-valence $Mn_2^{III,IV}$ complex is electrochemically generated. This latter complex can also be generated by electrolysis of the initial Mn_2^{II} complex in the presence of an external base, 2,6-lutidine (B).

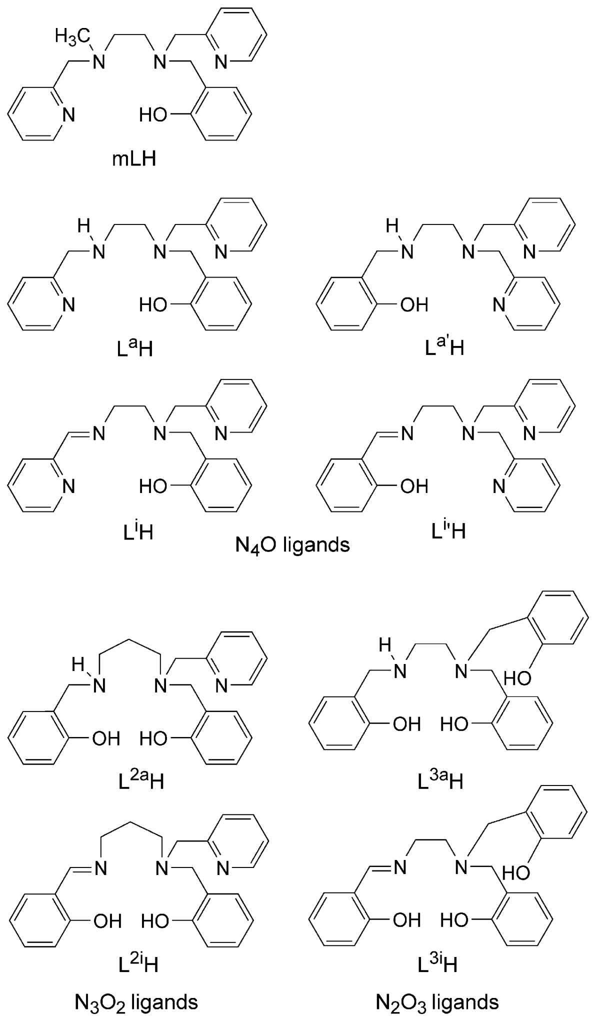


Figure 13. Schematic representation of pentadentate N_4O, N_3O_2 and N_2O_3 phenolic ligands.

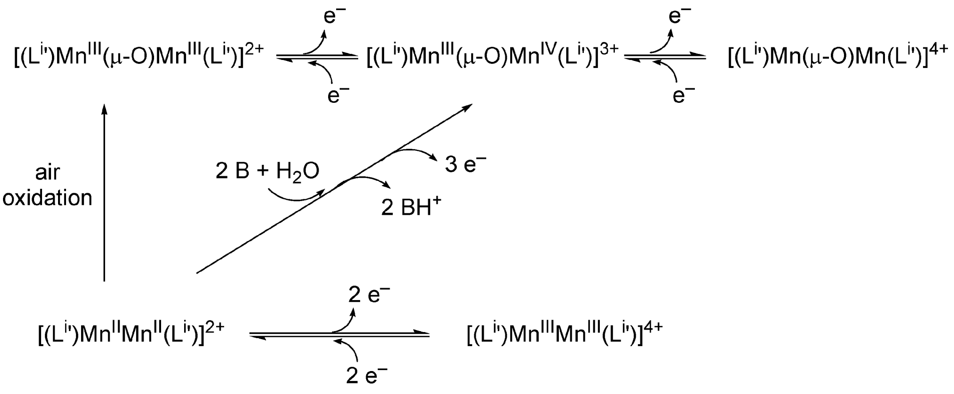
Table 6. Cyclic voltammetry potentials vs. SCE in CH_3CN for dinuclear complexes containing a Mn_2^{II}(μ-phenoxido)$_2$ core and a Mn_2^{III}(μ-O) core with pentadentate N_4O ligands.

Complex	$E_{1/2}$ [V] (ΔEp [mV]) Mn_2^{III}/Mn_2^{II}	$Mn_2^{III,IV}/Mn_2^{III}$	Ref.
$[L^{i\prime}Mn^{II}Mn^{II}L^{i\prime}]^{2+}$	0.46 (133)	1.42^{irrev}	[145]
$[(L^i/L^a)Mn^{II}Mn^{II}(L^i)]^{2+}$	0.89, 1.02[a]		[146]
$[(mL)Mn^{II}Mn^{II}(mL)]^{2+}$	0.58 (260)		[147]
	$Mn_2^{III,IV}/Mn_2^{III}$	$Mn_2^{IV}/Mn_2^{III,IV}$	
$[Mn_2^{III}O(L^{i\prime})_2]^{2+}$	0.55 (92)	1.0 (91)	[143]
$[Mn_2^{III}O(mL)_2]^{2+}$	0.65 (135)	1.16 (100)	[147]

[a] The two potential values correspond to the sequential one-electron oxidation of the Mn_2^{II} complex leading to the Mn_2^{III} complex. Irrev: irreversible process, the potential given corresponds to the *E*p value.

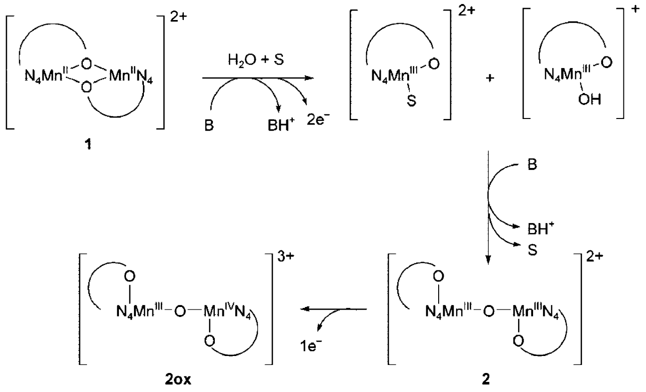
The manganese coordination is markedly different with L^aH; the other ligand contains an NH group (Figure 13). A mononuclear complex $[Mn^{III}(L^a)(O_2CCH_3)]^+$ has been synthesised by reaction with $Mn^{III}(O_2CCH_3)_3{\cdot}2H_2O$. However, in an CH_3CN solution this complex spontaneously evolves into a mixture of phenolato-bridged Mn_2^{II} dinuclear complexes, $[(L^i)Mn^{II}Mn^{II}(L^i)]^{2+}$ and $[(L^a)Mn^{II}Mn^{II}(L^i)]^{2+}$, with the concomitant oxidation of the ligand.[146] The CVs of these dinuclear complexes exhibit a quasi-reversible one-electron oxidation system attributed to a slow-electron transfer resulting from structural reorganisation. However, the final product of evolution of the transient $Mn_2^{II,III}$ species has not been identified.

A similar dinuclear complex, $[(mL)Mn^{II}Mn^{II}(mL)]^{2+}$ (**1**), has been synthesised with the mL ligand (Figure 13).[147] This compound furnishes another important and significant example of well-characterized, electroinduced formation of a μ-oxido dinuclear manganese complex. The CV of **1** exhibits two close irreversible oxidation peaks in CH_3CN attributed to its two-step oxidation into an unstable $[(mL)Mn^{III}Mn^{III}(mL)]^{3+}$ species (Table 6). However, exhaustive electrochemical oxidation in the presence of a base [2,6-lutidine (B)] allows the formation of the μ-oxido mixed-valent $[(mL)Mn^{III}(O)Mn^{IV}(mL)]^{3+}$ (**2ox**) derivative. The proposed mechanism is shown in Scheme 10. The initial step consists of a one-electron oxidation per Mn atom that leads to the breaking of the phenolato bridges and the generation of a



Scheme 9. Scheme of the various chemical or electrochemical reactions involved between complexes with the $L^{i\prime}$ ligand, adapted from ref.[143,145]

hydroxido mononuclear Mn^{III} species. The condensation of two Mn^{III} species in basic medium gives the μ-oxido dinuclear $[(mL)Mn^{III}(O)Mn^{III}(mL)]^{2+}$ (**2**) complex, which is oxidised into its mixed-valent state **2ox** at the potential of the electrolysis. It should be noted that chemical oxidation by *t*BuOOH transforms **1** into **2**, which partially evolves into the di-μ-oxido species $[(mL)Mn^{III}(O)_2Mn^{IV}(mL)]^{n+}$ in which one of the aromatic rings of the ligands is decoordinated. Oxidation of **1** by iodosylbenzene (PhIO) in methanol leads to the quantitative formation of the mononuclear $[Mn^{III}(mL)(OCH_3)]^+$ complex, which can be further electrochemically oxidized into $[Mn^{IV}(mL)(OCH_3)]^{2+}$.[148]



Scheme 10. Proposed mechanism for the electrochemical formation of **2ox** (the figure was reproduced from ref.[147], with permission from Wiley).

N_3O_2 and N_2O_3 Ligands

There are few studies of complexes of these kinds of ligands. By using a diphenolate pentadentate $L^{2a}H$ ligand (N_3O_2) (Figure 13), a trinuclear di-μ-phenolato μ-carboxylato $[(L^{2a})Mn^{III}(OCCH_3)Mn^{II}(OCCH_3)Mn^{III}(L^{2a})]^{2+}$ complex has been synthesised. This compound is irreversibly oxidized in CH_3CN into an unidentified product while its chemical oxidation in the same solvent by *t*BuOOH leads to the formation of the mononuclear Mn^{IV} hydroxido species, $[Mn^{IV}(L)(OH)]^+$ (L = L^{2a} and L^{2i}) identified by EPR spectroscopy and ESI-mass spectrometry.[149] Reaction of a trisphenolato $L^{3a}H$ ligand (N_2O_3) with $Mn^{III}(O_2CCH_3)_3·2H_2O$ produces the mononuclear pentacoordinate $[Mn^{III}(L^{3i})]$ complex. Upon one-electron oxidation (the process is irreversible in the CV) a Mn^{IV} species is formed that is partly converted to another species containing a loosely coordinated phenoxy radical and further oxidation results in an over-oxidation of the ligand. Attempts to observe an oxido–Mn species by oxidation with PhIO were unsuccessful, although epoxidation reactions occurred.[150]

Concluding Remarks

This review gives an overview of literature studies dedicated to electro- and photoinduced formation and transformation of oxido-bridged multinuclear manganese complexes. If these kinds of studies were initiated as early as the end of the seventies with polypyridyl complexes, a large expansion of this field has occurred over the last ten years because of the motivation to mimic redox-active manganese metalloenzymes. The majority of the studies have been performed in an organic medium (CH_3CN) and are related to dinuclear complexes. Oxido-bridged high-valent dinuclear manganese complexes with core types $\{Mn^{III}(O)Mn^{III/IV}\}$ and $\{Mn^{III/IV}(O)_2Mn^{IV}\}$ have been generated from the oxidation of low valent complexes; mononuclear and dinuclear μ-acetato/μ-phenolato-bridged. In contrast, only a few studies are related to aqueous solutions and in this particular case the formation of oxido-bridged tetranuclear complexes has been obtained. The strong electronegative donor properties of the oxido bridge encourage the high-valent manganese species to aggregate preventing the formation of a terminal oxido ligand.

The formation of oxido bridges in response to Mn oxidation likely involves (*de*)protonation events [of water molecule(s)]. In pure CH_3CN, to reach a high yield for the formation of oxido-bridged species it appears that the presence of an added base is required in order to capture the protons released during the oxidation process. For acetato complexes, the acetate anions released during the oxidation process play the role of the base. In pure aqueous solution or in CH_3CN, containing a large amount of water, the presence of an additional base is not necessary.

The formation of oxido bridges also prevents a potential increase, for example the typical $Mn_2^{III,IV}/Mn_2^{IV,IV}$ for a di-μ-oxido dinuclear complex does not exceed 1.3 V vs. SCE.

Finally, it appears as a general rule that the oxidation of Mn leads to the formation of very stable oxido-bridged species and to date, in contrast to ruthenium complexes, to the best of our knowledge, no example of electrochemical generation of Mn complexes with a terminal oxido ligand has been published. Theses kinds of complexes are rare and formation of such species will bring some insight into the mechanism of oxygen–oxygen bond formation in PSII. The design of such manganese complexes remains an important challenge for finding an efficient water oxidation catalyst.

Acknowledgments

The authors gratefully thank their students and coworkers whose names appear in the references cited, Dr. J.-M. Latour and Dr. C. Duboc for their collaborations and contributions and Dr. A. Blackman for a critical reading of the manuscript. This work is funded in part by the Agence Nationale pour la Recherche (Grant No. ANR-05-JCJC-0171-01) and was supported in part by the COST D21, Action "Metalloenzymes and Chemical Biomimetics".

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Received: November 23, 2008