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Implications of remote water molecules on the electron transfer coupled processes at a nonporphyrinic Mn(III)-hydroxido complex†

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Electrochemical studies of a new Mn(III)(OH) complex clearly evidence that the presence of outer spheres water molecules is essential for the reversibility of $Mn^{III/II}$ and $Mn^{IV/III}$ redox processes. In the $Mn^{III/II}$ case we found an isotope effect for D_2O and $^{18}OH_2$ allowing us to propose a mechanism for H_2O/HO^- ligand exchange coupled electron transfer activation of $Mn–OH_2$

Nature uses a Mn_4Ca cluster, known as the Oxygen Evolving Complex (OEC) buried in Photosystem II to remove electrons and protons out of water which are then used to fix carbon dioxide.[1,2] Understanding and replicating how nature performs the four-electron four-proton oxidation of water are attracting an unprecedented interest.[3–5] There are still several enigmas in the mechanism for the water oxidation. One consensus concerns the participation of highly oxidised manganese-oxo species in the oxygen–oxygen bond formation.[6–8] However, processes such as proton transfer and concerted proton electron transfer are acknowledged to be crucial in the water oxidation at the OEC.[9–12] A structural requirement in the convoy of the protons is the short-range interaction allowing delivery over long distances. Pioneering work from Wydrzynski and colleagues has shown that water exchange occurs in all the oxidation states at the Mn_4Ca cluster.[13] It is then very likely that water molecules in the close sphere are the first concerned in the proton equilibration.

Studies on manganese synthetic compounds can help to better understand the discrete activation steps in the water oxidation reaction. Formation of Mn-oxo species by water activation has not been studied in detail yet. In their vast majority these species have been generated by oxygen-containing oxidants until recently, where they were chemically or electrochemically generated from a bound substrate water molecule.[14–16] Therefore little is known to date on the microscopic steps upon water activation at a manganese centre. We report here on the synthesis and characterisation of a mononuclear manganese(III) complex surrounded by a $[N_4O]$ pentadentate ligand shaped with encumbered groups and leaving a free site for a substrate water molecule. The electrochemical behaviour of the Mn(III)–OH derivative clearly points out that the presence of water is playing a key role in redox processes of both the $Mn^{III/II}$ and $Mn^{IV/III}$ couples. We also observed a kinetic isotope effect (KIE) on the $Mn^{II}OH/Mn^{II}OH_2$ proton transfer process with both D_2O and $H_2{}^{18}O$ allowing us to propose a proton transfer mechanism combined to a water molecule exchange at a manganese based complex.

Broader context

Understanding how nature uses a Mn_4Ca (the Oxygen Evolving Complex in Photosystem II) to perform the four-electron four-proton water oxidation on one side and how to duplicate these events in robust synthetic systems on the other are gathering an unprecedented effort from the scientific community. Although, different molecular systems have been reported as potential water oxidising catalysts, no well-established approach using first row transition elements performing the four-electron oxidation of water has been set to date. We report here on the electrochemical activation of a manganese bound water molecule and we unravel how buzzing water molecules outside the coordination sphere play an essential role in inhibiting the formation of the trivial μ-oxo polymanganese complexes and also participate in the water exchange at the manganese centre. These results can help to understand the basic steps in the water oxidation process.

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The mononuclear Mn(III) complex [*t*BuLMn(III)OH](ClO$_4$) (**1** (ClO$_4$)) was prepared following a template synthesis in ethanol, with [Mn(II)(OH$_2$)$_6$](ClO$_4$)$_2$ as a source of manganese. Crystals of sufficient quality were obtained for X-ray analysis (Fig. 1). A unique feature of the structure of **1**$^+$ is the existence of water molecules in hydrogen bonding distances with the metal bound OH group. However, owing to some disorder of the water molecules, two structural motifs were found in the unit cell. Each Mn(III) ion is wrapped by the pentadentate N$_4$O ligand and an HO$^-$ ligand completes the coordination sphere. Main structural differences reside in the Mn–OH bond lengths at 1.86(3) and 1.97(3) Å and the distribution pattern of the surrounding water molecules (see Fig. S1†). Snapshots of the closest HO···OH$_2$ distances of 2.60(5) and 2.85(2) Å for each unit respectively attest for hydrogen bonding interaction. Also, the mean intermolecular distances between contiguous water molecules are in favour of a stable hydrogen-bonding network. To the best of our knowledge, we are unaware of such structural features in molecular Mn(III) hydroxide complexes. We view this as an interesting piece of information related to the water/hydroxido exchange mechanism and may also point to possible proton exit pathways from the metal bound substrate water molecule either in the OEC or in synthetic systems. Of note, the Jahn–Teller distortion axis is observed along the N$_{\text{pyridine}}$–Mn–N$_{\text{pyridine}}$ axis while the Mn$^{\text{III}}$-OH bond lengths are somewhat longer than those previously reported.[16–20]

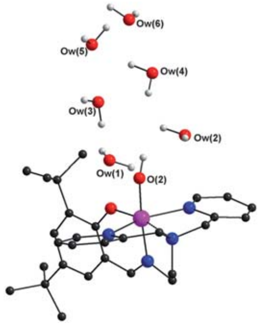


Fig. 1 X-Ray crystal view of **1**$^+$ showing HO$^-$ in hydrogen bonding with water molecules. Protons on the ligand are omitted for clarity and protons on the water molecules were placed within restricted bond distances. Selected distances for one of the sites are as follows: Mn–O(2) 1.86(3), O(2)–Ow(1) 2.75(8), O(2)–Ow(2) 2.60(5), Ow(1)–Ow(3) 3.73(3), Ow(3)–Ow(5) 2.76(5), Ow(2)–Ow(4) 3.15(2), Ow(4)–Ow(6) 2.50(5), Ow(5)–Ow(6) 2.47(1).

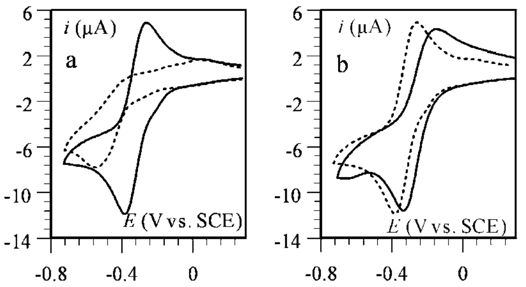


Fig. 2 Cyclic voltammetry of **1**$^+$ (1 mM) at 0.1 V s^{-1}, $T = 293$ K, on a glassy carbon electrode in CH$_3$CN + 0.1 M NBu$_4$PF$_6$. (a) dashed line: **1**$^+$ in dry solvent; full line: **1**$^+$ + 10 M H$_2$O. (b) Dashed line: **1**$^+$ + 10 M H$_2$O, full line: **1**$^+$ + 20 M H$_2$O.

The characterized complex **1**$^+$ hereafter named [Mn(III)OH]$^+$ was then studied by cyclic voltammetry. In dry acetonitrile, its reduction leads to a chemically irreversible wave (Fig. 2a, dashed line). Comparison with a monoelectronic reversible wave obtained with a complex of similar size indicates that the stoichiometry of the wave is less than one electron. This evidences a chemical reaction coupled to the electron transfer involving a father–son (Mn(III)–Mn(II)) process. We thus suggest a mechanism for which the reduction of [Mn(III)OH]$^+$ is followed by the formation of a dinuclear species. EPR spectra recorded on an electrolysed solution at −0.64 V *vs.* SCE bring evidence for this statement (see Fig. S2†). Formation and characterization (structural and spectroscopic) of Mn(II) dinuclear complexes with similar [N$_4$O] ligand have been reported previously.[21,22] More interestingly, the addition of water (up to 10 M) leads to a positive shift of the cathodic wave,‡ to an increase in the cathodic current and the chemical reversibility of the wave (Fig. 2a, full line). Based on these electrochemical responses, we attribute the reversible wave to the following mechanism where electron transfer is coupled to a fast equilibrium (2) therefore preventing the formation of the dinuclear species.

$$\left[\mathrm{Mn^{III}OH}\right]^{+} + \mathrm{e}^{-} \rightleftharpoons \left[\mathrm{Mn^{II}OH}\right] \qquad (1)$$

$$\left[\mathrm{Mn^{II}OH}\right] + \mathrm{H_2O} \rightleftharpoons \left[\mathrm{Mn^{II}OH_2}\right]^{+} + \mathrm{OH}^{-} \qquad (2)$$

All attempts to isolate the [LMn(II)(OH$_2$)]$^+$ species by reductive electrolysis of [LMn(III)(OH)]$^+$ in the presence of water were unsuccessful. The aqua species [LMn(II)(OH$_2$)]$^+$ is thus corroborated only on the cyclic voltammetry time-scale. Reaction (2) is basically a proton exchange (acid–base reaction) hence the whole sequence can be described as a formal proton coupled electron transfer process. The hydroxide ligand bound to a Mn(II) cation being a weaker base than free HO$^-$ renders the equilibrium (2) thermodynamically unfavourable (the equilibrium constant $K_{1\text{-}2}$ being <1). However, addition of a larger amount of water (from 10 to 20 M) shifts the equilibrium towards the formation of [Mn(II)OH$_2$]$^+$ as a product. The shape of the voltammogram is therefore modified as a consequence of the kinetic interference of reaction (2). This is neatly pointed out in Fig. 2b with the loss of reversibility and a broadening of the anodic wave with increasing the amount of added water. These experimental observations evidence that reaction (2) is no more at equilibrium[23] (see ESI†).

Therefore, the shape of the anodic wave is now kinetically partially controlled by reaction (2). Experiments performed in the presence of D$_2$O and ^{18}OH$_2$ show a clear kinetic isotope effect (KIE) in both cases (Fig. 3). Interestingly, a stronger effect is observed in the case of ^{18}OH$_2$ (a), than in the case of D$_2$O (b). Since primary kinetic isotope effects are stronger for hydrogen than oxygen, our findings suggest that the observed KIE is primary for oxygen and secondary for hydrogen. These results lead us to propose that a Mn–O bond is broken in the course of the reaction (2), thus supporting a ligand exchange rather than a simple proton transfer.

Scheme 1 adapts a possible scenario to describe the observed kinetic isotopic effects together with an exchange of water molecules in the coordination sphere of manganese. A clear-cut fact is that water is playing a crucial role in this process. Based on the X-ray data of **1**$^+$, we positioned three water molecules in the vicinity of the metal bound HO$^-$ as shown in Scheme 1.

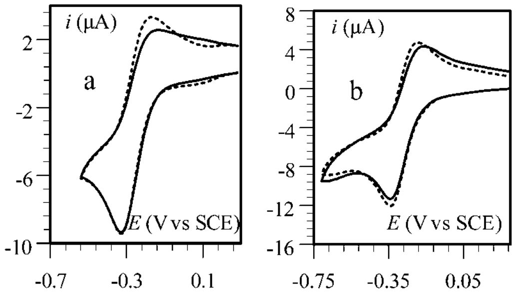


Fig. 3 Cyclic voltammetry of 1^+ at 0.1 V s^{-1}, $T = 293$ K, on a glassy carbon electrode in CH_3CN + 0.1 M NBu_4PF_6 (a) dashed line: in the presence of 10 M of H_2O; solid line: in the presence of 10 M of $^{18}OH_2$. (b) Dashed line: in the presence of 10 M of H_2O; solid line: in the presence of 10 M of D_2O; KIE (H/D) $\approx$2; KIE ($^{16}O/^{18}O$) > 5 (see ESI†).

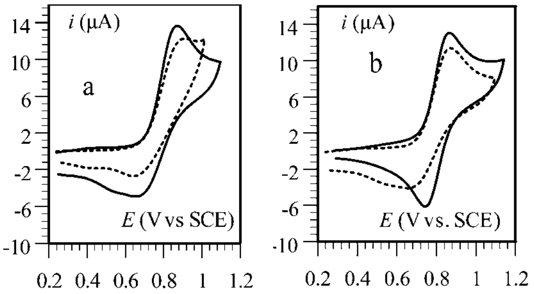
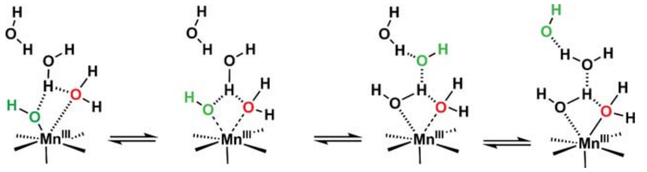


Fig. 4 Cyclic voltammetry of 1^+ (1 mM) at 0.1 V s^{-1}, $T = 293$ K, on a glassy carbon electrode in CH_3CN + 0.1 M NBu_4PF_6 (a) in dry solvent (solid line) and in the presence of 132 mM of 2,6-dimethylpyridine (dashed line). The anodic peak is not well defined due to the proximity of a catalytic oxidation peak of 2,6-dimethylpyridine; (b) 1^+ (1 mM) in dry CH_3CN (dashed line) + 13 M of H_2O (solid line).



Scheme 1 Proposal for the sequential steps accounting for the HO^-/H_2O ligand exchange according to the observed O^{16}/O^{18} and H/D KIE. The solid line represents the actual bonding interaction and dotted line the weak interaction. Red oxygen belongs to the closest second sphere water molecule and green HO^- ion represents the hydroxide shifting from the Mn ion.

A water molecule is placed close to the electrochemically generated Mn(II) ion and two further others within hydrogen bonding interaction distance. The closest second sphere water molecule (oxygen marked in red) is involved in the water exchange process while the other two act literally as proton donor to the bound OH group following a Grotthuss-like mechanism.[24] Put differently, this process is the mere shifting of the HO^- ion away from the metal centre (in green in Scheme 1).

After having analysed the Mn(II)OH_2/Mn(III)OH proton coupled electron transfer we will now investigate the Mn^{III}/Mn^{IV} redox process. In dry acetonitrile, oxidation of 1^+ gives a monoelectronic anodic wave not fully reversible. Addition of a large amount of base (2,6-dimethylpyridine) increases the chemical irreversibility and induces a decrease of the anodic current corresponding to a decrease of the electron stoichiometry (Fig. 4a).

This behavior is attributed to the classical formation of manganese μ-oxo dimers as previously described[25–27] and is translated by eqn (3) and (4). Control EPR experiments on an electrolysed solution confirmed this statement (see Fig. S4†). It is to be noted that even the presence of the bulky *tert*-butyl group in the close proximity of the Mn–OH fragment does not inhibit the formation of the μ-oxo dimer under such conditions.

$$[\mathrm{Mn^{III}OH}]^{+} \rightleftharpoons [\mathrm{Mn^{IV}OH}]^{2+} + e^{-} \qquad (3)$$

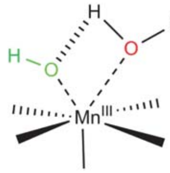
$$[\mathrm{Mn^{IV}OH}]^{2+} + [\mathrm{Mn^{III}OH}]^{+} \rightleftharpoons [\mathrm{Mn^{IV}\text{-}O\text{-}Mn^{III}}]^{3+} + H_2O \qquad (4)$$

More intriguingly, we found that upon addition of a large amount of water (up to 25% in volume, 13 M) and in the absence of a base, the electrochemical reversibility of the Mn(III)/Mn(IV) process is restored (Fig. 4b). Referring to eqn (4) this may be inferred to a shift of the equilibrium towards the monomeric product $[\mathrm{Mn^{IV}OH}]^{2+}$ or rather, the presence of water molecules in the second coordination spheres prevents the condensation reaction between the $[\mathrm{Mn^{IV}OH}]^{2+}$ and the $[\mathrm{Mn^{III}OH}]^{+}$ species. We performed exhaustive bulk electrolysis of 1^+ at 1 V *vs.* SCE in the presence of water. Controlled potential coulometric measurements confirmed a one-electron oxidation process per manganese ion and the cyclic voltammogram recorded on the electrolysed solution of 1^+ shows a trace that is identical to one of the initial solutions pertaining the chemical reversibility of the oxidized species (see Fig. S5†). EPR spectra recorded on aliquots of the electrolysed solution confirm the presence of a genuine high spin Mn(IV) species (see Fig. S6†). No isotopic effect was detected when running the electrochemical studies in the presence of D_2O or $^{18}OH_2$ (see Fig. S7 and S8†). These experimental features tend to confirm a simple electron transfer from $[\mathrm{Mn^{III}OH}]^{+}$ species that is not coupled with deprotonation at the level of Mn^{IV} species. As already mentioned, a first attempt to describe the role of the surrounding water molecules is to visualize them acting as a shield to inhibit the condensation reaction. But the role of water molecules is probably more intimate because they are also involved in a dynamic equilibrium at the level of the starting Mn^{III} species. Indeed, mass spectrometry experiments on complex 1^+ show $^{18}O/^{16}O$ exchange (see Fig. S3†), thus emphasizing the lability of OH/H_2O ligands on the Mn(III) cation as recently shown on water–ligand exchange in Mn(III) porphyrins.[28] In the present case the isotope exchange (eqn (5)) is formally a ligand exchange (eqn (6)) coupled to a deprotonation process (eqn (7)).

$$\begin{tikzcd}
{[\mathrm{Mn^{III}OH}]^{+} + H_2O^{*}} \arrow[rr, leftrightharpoons] \arrow[dr, leftrightharpoons, "(6)"'] & & {[\mathrm{Mn^{III}O^{*}H}]^{+} + H_2O} & (5) \\
& {[\mathrm{Mn^{III}O^{*}H_2}]^{2+} + HO^{-}} \arrow[ur, leftrightharpoons, "(7)"'] & &
\end{tikzcd}$$

Nevertheless, such a mechanism can be ruled out based on the following considerations. Trivial thermodynamics cycle gives:

$$\log K_{3-2} = \frac{F\left(E^0_{\mathrm{Mn^{III}OH+H_2O/Mn^{II}OH_2+OH^-}} - E^0_{\mathrm{Mn^{III}OH_2/Mn^{II}OH_2}}\right)}{RT\ln 10}$$



Scheme 2 Proposed representation of the Mn(III) species loose structure in solution.

In the presence of a strong acid we observe that $E^0_{Mn^{III}OH_2/Mn^{II}OH_2} = 0.32$ V *vs.* SCE (see Fig. S13†). Moreover, in the presence of water (10 M), as shown in Fig. 2a, we measure $E^0_{Mn^{III}OH+H_2O/Mn^{II}OH_2+OH^-} = -0.35$ V *vs.* SCE. This leads to log $K_{3-2} = -11.15$. We can thus conclude that the oxygen isotope exchange reaction (eqn (5)) may certainly not be decomposed into two reactions ((6) and (7)) going through the high energy intermediate $[Mn^{III}OH_2]^{2+}$. Therefore, we have to consider another pathway: for instance a concerted ligand exchange and deprotonation or formation of a species where both HO^- and H_2O are ligated with an internal proton transfer again emphasizing the lability of OH/H_2O ligands on Mn(III) cations. While this reaction *per se* cannot kinetically interfere in the Mn^{III}/Mn^{IV} redox process, it points out that the Mn^{III} coordination sphere is flexible and that the second coordination sphere ligands have to be considered for the description of the Mn(III) species reactivity. In other words this Mn(III) species may not be viewed as a simple hydroxide anion tightly bound to the Mn(III) but rather as a loose structure as depicted in Scheme 2.

This may influence the dynamics of electron transfer which is the rate determining step in the Mn^{III}/Mn^{IV} redox process as indicated by the quasireversible behaviour observed for the oxidation wave of complex **1**$^+$ in the presence of water (potential peak separation is 200 mV at a scan rate 0.1 V s^{-1}). These observations call for further investigations of electron transfer dynamics to decipher intrinsic parameters of the Mn^{III}/Mn^{IV} redox process. These studies are in progress in our labs.

Conclusions

We have reported here on some original aspects in the electron transfer processes at a Mn(III)OH complex. We have found that exogenous water molecules can steer the reversibility of the $Mn^{II}/^{III}$ and $Mn^{III/IV}$ redox processes thereby inhibiting the formation of undesired μ-oxo compounds. Cyclic voltammetry in conjunction with H/D and $^{18}O/^{16}O$ kinetic isotopic effects analyses evidence a H_2O/HO^- ligand exchange process preceding electron transfer for the $Mn^{II/III}$ couple. No such KIEs are observed in the case of the $Mn^{III/IV}$ couple, for which the electron transfer occurs without proton loss, thus allowing the formation of a genuine Mn(IV)OH species in the presence of water. The present work evidences the role of H_2O/HO^- ligand exchange dynamics coupled with change of oxidation state in manganese chemistry. We believe that such a ligand exchange coupled electron transfer (LECET) has to be considered upon investigation of the water activation by Mn complexes. An underlying question that remains to be answered is that of the effects of the second sphere water molecules on the dynamics of electron transfer, a key step to activate a water molecule.

Acknowledgements

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Notes and references

‡ When necessary, potentials have been corrected for the shift induced by modification of the junction potential upon water addition (see ESI†).

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