Single Electron Transfer Steps in Water Oxidation Catalysis. Redefining the Mechanistic Scenario

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ABSTRACT: The systematic computational study of the mechanism for water oxidation in four different complexes confirms the existence of an alternative mechanism to those previously reported: the single electron transfer - water nucleophilic attack (SET-WNA). The new

mechanism relies on two SET steps, and features the existence of an intermediate with a (HO•••OH)-moiety attached to the metal center. It is operative in at least three representative copper based complexes, and is the only option that explains the experimentally observed efficiency in two of them. The proposal of this new reaction pathway redefines the mechanistic scenario and importantly, generates a completely new avenue for designing more efficient water oxidation catalysts based on first row transition metals.

Introduction

Water splitting driven by sunlight to produce molecular oxygen and hydrogen is regarded as one of the most promising approaches for the generation of clean fuels in a sustainable manner.[1,2] Hydrogen generated in this manner is generally labeled as solar-hydrogen[3] and is regarded as a way of storing solar energy into chemical bonds, in similar manner as done by the photosystem II of green plants and algae.[4]

From an electrochemical perspective the water splitting reaction consists in two half reactions: water oxidation to molecular oxygen and proton reduction to hydrogen. Particularly the water oxidation to dioxygen has been traditionally regarded as the bottleneck for the design of practical devices that can carry out water splitting with sunlight.[5-8]

The water oxidation to dioxygen reaction, besides being energy demanding ($E^o = 1.23$ V vs NHE at pH = 0), is also molecularly complex since requires the break of four H-O bonds, the releasing 4 electrons and 4 protons together with the formation of an O-O bond. This complex mechanistic scenario generally translates into very high over-potentials needed for the reaction to proceed.[9]

One of the potential strategies to overcome high activation energies consists in the involvement of transition metals as catalysts. Indeed a number of Ru[10-17] and Ir[18-22] complexes have been recently described as efficient catalysts for this reaction. Furthermore the understanding of the different mechanisms involved in these catalytic processes as well as the potential deactivation pathways, has been crucial for the development of the field. However better catalysts, more robust and efficient, are needed to be able to incorporate them in devices that can carry water splitting with sunlight.

In order to progress in this front it is essential to gain a deeper understanding of the reaction mechanisms that can operate in water oxidation catalysis. From this perspective it is imperative to spectroscopically characterize reaction intermediates as well as their reactivity. In this respect the theoretical methodologies become an extremely valuable tool to complement experimental work, especially in systems with such a complexity as the water oxidation reaction catalyzed by transition metals.

Mechanistic and theoretical studies have been carried out mainly with Ru complexes and have led to propose two main pathways for the O-O bond formation step depending on whether an external water molecule is involved or not. Thus a water nucleophilic attack (WNA) and interaction of two M-O species (I2M) have been extensively discussed by our group and others.[23,24]

Transition metals in their high oxidation states containing the M-O group can be described using two resonant forms depending on whether the oxidation occurs solely at the metal center or at the oxygen, as depicted on the left hand side of Figure 1. All over the present paper we will

use formal oxidation states since this allows easily tracking electron trafficking, although it is obvious that the real species will be a mixing of both resonant forms.

A WNA mechanism (Figure 1) is found when the auxiliary ligands favor the stabilization of the oxo form shown on Fig. 1 top and an I2M mechanism is found when the favored species resemble those of the oxyl radical form depicted in the lower part of Figure 1. The WNA involves a concerted two electron process from the incoming water molecule to the metal center of the M-oxo group resulting in the formation of a peroxide intermediate and the reduction of the metal center by two units. On the other hand the I2M mechanism involves a radical coupling where the oxidation state of the metal center remains unchanged.
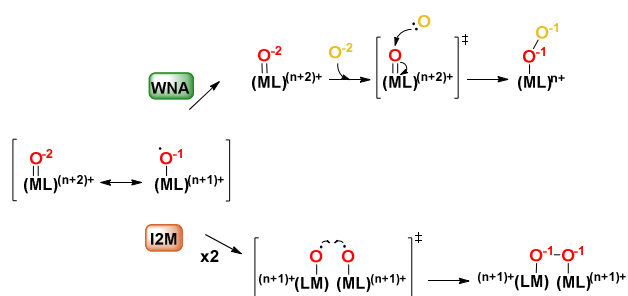

Figure 1. Schematic view of Water Nucleophilic Attack (WNA) and Interaction of Two M-O Species (I2M) mechanisms. Formal oxidation states for the metal and oxygen atoms are indicated as superscript.

Recently several first row transition metal complexes have been reported as catalysts for the water oxidation reaction.[25-40] While these catalysts are of interest because of their high abundance and low toxicity, their performance is much poorer than their Ru or Ir analogues, and in addition their mechanistic pathways are in most cases basically unknown.[28-30,41-43]

We have very recently reported a new complex based on Cu, containing the amidate ligand OPBAN that can carry out the water oxidation reaction in a very efficient manner. Surprisingly from a mechanistic perspective it does not follow the WNA or I2M schemes just described but rather a step by step one electron process that we have termed SET-WNA. Incidentally in parallel there is an increasing recognition of the presence of single electron transfer (SET) steps in first-row homogeneous catalysis.[45,46]

Therefore, it seems necessary and reasonable to raise these approaches to water oxidation catalysis using first row transition metals with the final aim of proposing a reasonable and complete mechanistic scenario.

The present woks thus aims at the description of a complete and integrated view of all the potential pathways leading to low energy O-O bond formation by transition metal catalysts.

Herein, we present a comprehensive DFT study on the water oxidation mechanism, with special attention to emerging copper catalysis that allows us to map the different accessible O-O bond formation pathways that in turn reveal the most important features for WO catalyst design.
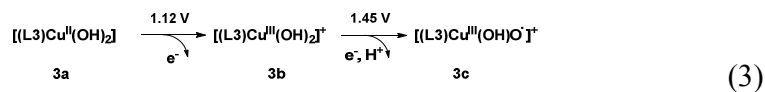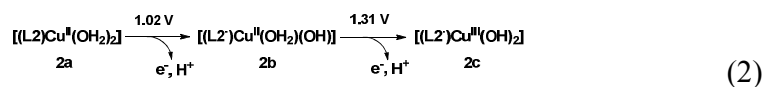
Results and Discussion

1. The SET-WNA mechanism in copper systems: $[(OPBAN)Cu^{II}]^{2-}$, $[(6,6'\text{-}dhbp)Cu^{II}(OH_2)_2]^{2-}$, $[(bpy)Cu^{II}(OH)_2]$

We first proposed the existence of a single electron transfer - water nucleophilic attack (SET-WNA) mechanism in a joint experimental and computational communication on $[(OPBAN)Cu^{II}]^{2-}$ (OPBAN= o-phenylenebis-(oxamidate)) complex, hereafter $[(L1)Cu^{II}]^{2-}$, **1a**.[31] We will briefly recall and extend the results on this system here, and compare them with those on

other copper complexes that have been shown experimentally to efficiently catalyze water oxidation. The new complexes studied are $[(6,6'\text{-dhbp})Cu^{II}(OH_2)_2]^{2-}$, $(6,6'\text{-dhbp}=$ [2,2'-bipyridine]-6,6'-bis(olate)), hereafter $[(L2)Cu^{II}(OH_2)_2]$, **2a**,[30] and $[(bpy)Cu^{II}(OH)_2]$ (bpy= 2,2'-bipyridine), hereafter $[(L3)Cu^{II}(OH)_2]$, **3a**.[28]

The key intermediates computed oxidation sequence for the three complexes is shown in eqs. 1 to 3 below, respectively (the full set of accessible species is reported in the Supporting Information, Supplementary Figs. 1 and 2).

$$[(L1)Cu^{II}]^{2-} \xrightarrow[e^-]{0.53\,V} [(L1)Cu^{III}]^- \xrightarrow[OH^-]{1.26\,V} [(L1)Cu^{III}(OH)]^-$$
$$\text{1a} \qquad\qquad \text{1b} \qquad\qquad \text{1c}$$

$$\tag{1}$$

$$[(L2)Cu^{II}(OH_2)_2] \xrightarrow[e^-,\,H^+]{1.02\,V} [(L2^-)Cu^{II}(OH_2)(OH)] \xrightarrow[e^-,\,H^+]{1.31\,V} [(L2^-)Cu^{III}(OH)_2]$$
$$\text{2a} \qquad\qquad\qquad \text{2b} \qquad\qquad\qquad \text{2c}$$

$$\tag{2}$$

$$[(L3)Cu^{II}(OH)_2] \xrightarrow[e^-]{1.12\,V} [(L3)Cu^{III}(OH)_2]^+ \xrightarrow[e^-,\,H^+]{1.45\,V} [(L3)Cu^{III}(OH)O^-]^+$$
$$\text{3a} \qquad\qquad\qquad \text{3b} \qquad\qquad\qquad \text{3c}$$

$$\tag{3}$$
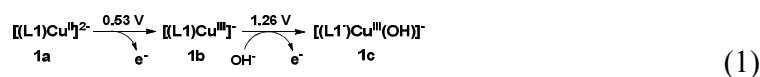
The active species is formed by two consecutive one electron oxidations that can be metal or ligand based. The highest potentials correspond to system **3**, where the L3 ligand is not oxidized since its redox potential is too high and thus the second electron is removed directly from the Cu-O moiety, forming an oxyl group, **3c**. In the other two systems the ancillary ligands acts as redox non-innocent. For **2**, the first step involves the removal of an electron from the ligand whereas this happens in the second step for complex **1**.

The set-up for the reaction between species **1c**, **2c**, **3c** with a hydroxyl/oxyl group bound to the metal and an external hydroxyl group, is typical of the WNA mechanism. But we did not find this mechanism to be preferred in any of the three cases. For the **1c/2c** complexes, we could not

locate a transition state connecting them directly to the resulting intermediates **1e**/**2e** (see Figure 2), where both oxygen atoms have a formal oxidation state of -1. The reason for this impossibility is apparent in the potential energy scans in the top part of Figure 2.

Intermediates **1c**/**2c** and **1e**/**2e** are at the bottom of two wells in red in the potential energy scan, and the energy of both curves increase sharply before they meet. Instead, the connection between the two intermediates takes place through an additional intermediate **1d**/**2d**, depicted in blue. This intermediate has a complex electronic structure as the unpaired electron is shared by both oxygen atoms, forming a 2c-3e⁻ bond[47] with a length around 2.30 Å. This bond has a formal order of 0.5 and a formal oxidation state of -1.5 in each oxygen atom (Figure S3).
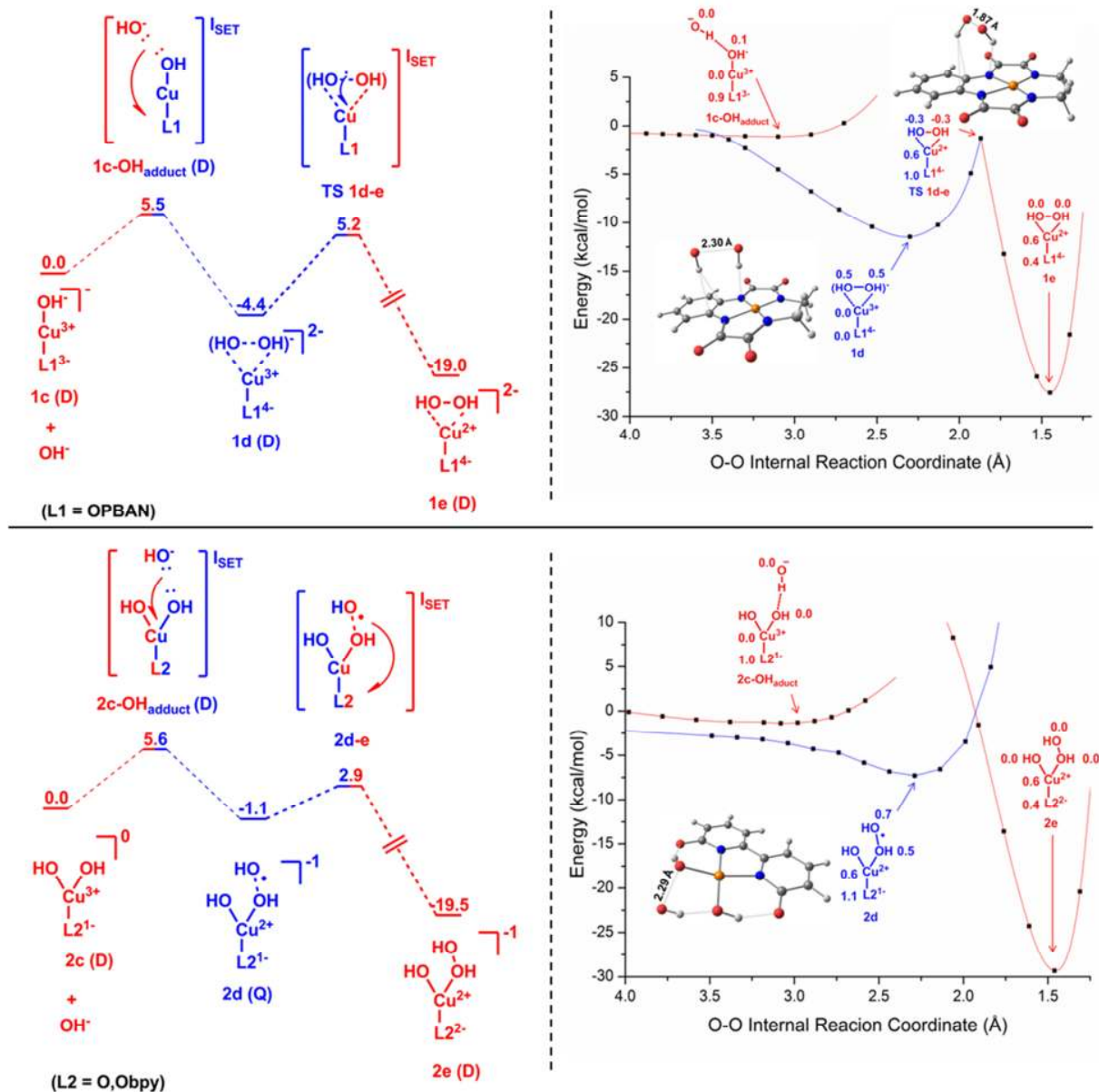
Figure 2. (Left) Free energy profiles of $[(L1)Cu^{II}]^{2-}$(top) and $[(L2)Cu^{II}(OH_2)_2]$ (bottom) where L1 = o-phenylenebis(oxamidate) and H2L2 = [2,2'-bipyridine]-6,6'-bis(olate)). Energies in kcal/mol. (Right) Potential energy relaxed scan of both complexes of the O-O reaction coordinate. The draw at right-top is based on one reported in ref. 31.

Intermediate **1d/2d** connects **1c/2c** to **1e/2e** through single electron transfer steps. The connection between **1c** and **1d** takes place through outer-sphere transfer, as the O-O distance is above 3.5 Å. There is no transition state in the potential energy surface for this step, but we could estimate a free energy barrier of 5.5 / 5.6 kcal/mol as the difference between a long-range adduct and the separate reactants. It is worth noticing that there is no crossing between the curves corresponding to **2c** and **2d** in the potential energy surface, but this has no significant effect on the reactivity, as the free energy of the separate reactants associated to **2c** becomes lower after introducing the entropic contributions. For the connection between **1d** and **1e**, we could locate the transition state **TS 1d-e** (Figure 3).
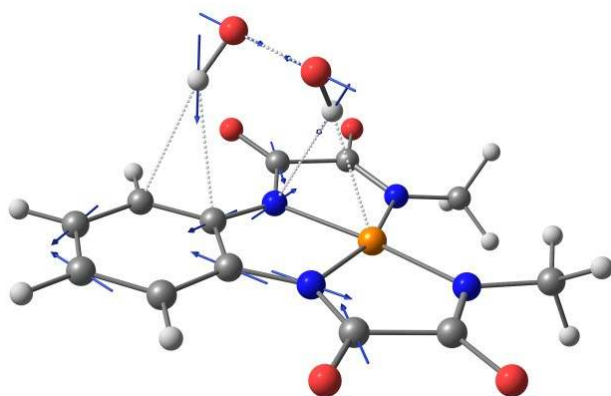

Figure 2. Displacement vectors of the reaction coordinate normal mode of **TS 1d-e**.

It contains an unpaired electron on the ligand (spin 1.0) and an additional open-shell between the copper (spin 0.6) and oxygen (spin -0.3 each) centers. This transition state has an energy 9.6 kcal/mol above intermediate **1d**. This constitutes the highest barrier in the process, which is thus obviously affordable at room temperature. Although the HO•••OH moiety is not attached covalently to the metal center (only by hydrogen bonds), the normal mode vectors show clearly the participation of the catalyst in the transition state. The connection between **2d** (quartet) and

2e(doublet) should take place through a minimum energy crossing point (MECP) which we could not locate for technical reasons, but we could estimate for it a low relative energy of 2.9 kcal/mol from the relaxed potential energy scan. The existence of states with different multiplicities can be in fact related to the concept of multi-state reactivity.[46] In spite of the minor differences between systems **1** and **2**, it is clear from Figure 2 that they share the same mechanism. We notice here that the possible intramolecular O-O bond formation process between the two hydroxyl ligands in **2c** was found to have a prohibitively high barrier (Figure S4).

A slightly different scenario is obtained for complex **3c**, where the ligand oxidation is very high in energy and thus is not oxidized. In this case, we could characterize an intramolecular WNA mechanism for O-O formation. The reductive coupling between the hydroxyl and the oxyl center can take place through a transition state **TS 3c-d'** that is 7.0 kcal/mol above **3c** (Figure S5). In this transition state, the O-O bond formation occurs simultaneously with the reduction of Cu^{III} to Cu^{II}. However the SET-WNA pathway involving an external hydroxyl group gives a lower barrier (Figure S6). Indeed, there is a $2c$-$3e^-$ O---O intermediate similar to those reported above, which evolves through a low energy path (Figure S6) towards the product. The highest point in this path is 3.6 kcal/mol above **3c**, thus significantly below the 7.0 kcal/mol reported above for the **TS 3c-d'** in the intramolecular WNA path.
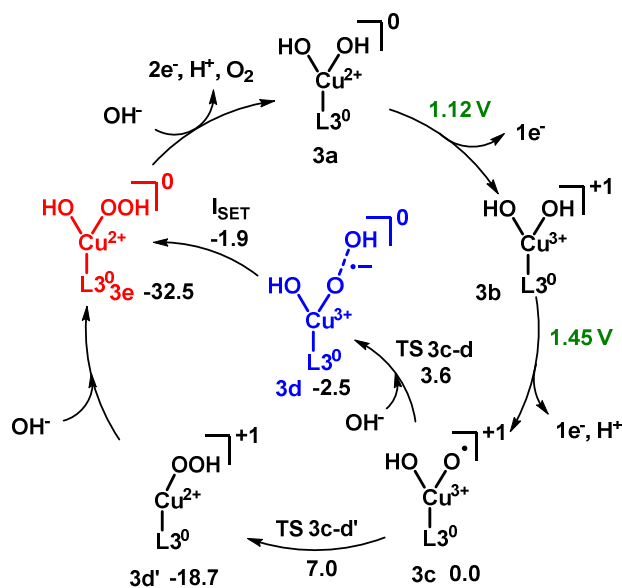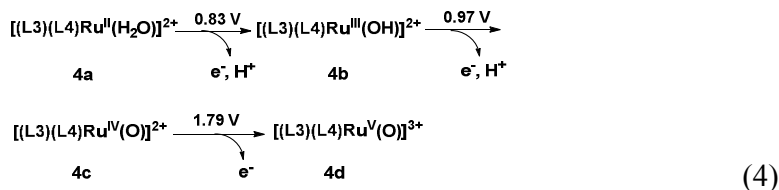
Figure 4. Catalytic cycle for $[(L3)Cu^{II}(OH)_2]$ complex where both the intramolecular WNA and intermolecular SET-WNA pathways are represented. Free energy changes for steps at the electrode are indicated explicitly in Volts (green) and for steps in solution are indicated in kcal/mol with respect to **3c** (black).

The two catalytic pathways just described for the $[(L3)Cu^{II}(OH)_2]$ complex are summarized in Figure 4. It is worth mentioning here that the low barrier obtained for the SET-WNA mechanism in this **3c** system is fully consistent with the reported turnover frequency of 100 s^{-1}, that is the highest described to date for Cu catalysts. More significantly, it confirms the prevalence of this type of mechanism for Cu-based water oxidation catalysts, even when the ligand is not involved in the redox process.

2. Extension to Ru systems? The case of $[(L3)(damp)Ru^{II}(H_2O)]^{2+}$

We finally explored how the SET-WNA mechanism could perform in cases where the conventional WNA mechanisms are well established. We chose the $[(L3)(damp)Ru^{II}(H_2O)]^{2+}$ (damp= 2,6-bis((dimethylamino)-methyl)pyridine) system, hereafter $[(L3)(L4)Ru^{II}(H_2O)]^{2+}$, that has been studied both experimentally and computationally.[14]

$[(L3)(L4)Ru^{II}(H_2O)]^{2+}$ $\xrightarrow[e^-, H^+]{0.83 \text{ V}}$ $[(L3)(L4)Ru^{III}(OH)]^{2+}$ $\xrightarrow[e^-, H^+]{0.97 \text{ V}}$

4a   **4b**

$[(L3)(L4)Ru^{IV}(O)]^{2+}$ $\xrightarrow[e^-]{1.79 \text{ V}}$ $[(L3)(L4)Ru^{V}(O)]^{3+}$

4c   **4d**   (4)

In eq. 4 we present the oxidation sequence that has been reported for this system. The active species **4d** can be viewed also as having a formal Ru^{IV} state, as there is a partial oxyl character (0.4 e- in the oxygen and 0.6 in the Ru). A conventional WNA transition state has been computationally reported for the interaction of this complex with an external water molecule with a relative free energy of 20.7 kcal/mol. In this transition state, a lone electron pair of water attacks the oxygen center on ruthenium, and leads to a hydroperoxyl intermediate, $[(L3)(L4)Ru^{III}(OOH)]^{2+}$, that further evolves to generate dioxygen after one electron oxidation.
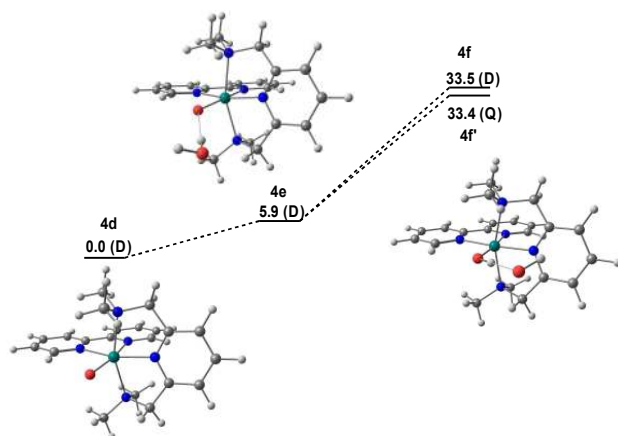

Figure 5. Free energy profile for the generation of Ru^{IV}-OH---HO• intermediate in $[(L3)(L4)Ru^{II}(H_2O)]^{2+}$.

An eventual SET-WNA mechanism from **4d** should go through an intermediate where an electron is transferred from the external water to the complex. We found this process to be not feasible and the results are summarized in Figure 5. An adduct between the complex and the external water can be found, but the intermediate with the 2c-3e⁻ bond between the two oxygen atoms is not formed. We tried to force this type of species with transfer of a H• radical from water to the catalyst (in a way analogous to the R-H activation chemistry previously reported by Neese and co-workers).[46] We could reach in this way the Ru^{IV} complex shown in Figure 4 (species **4f**). This complex, either in doublet or quadruplet state, has an energy more than 10 kcal/mol above the competing WNA transition state, most likely because the oxygen centered •OH radical is not sufficiently stabilized by the Ru-OH moiety. These results clearly indicate that the SET-WNA mechanism is not operative in the Ru WOC chemistry.

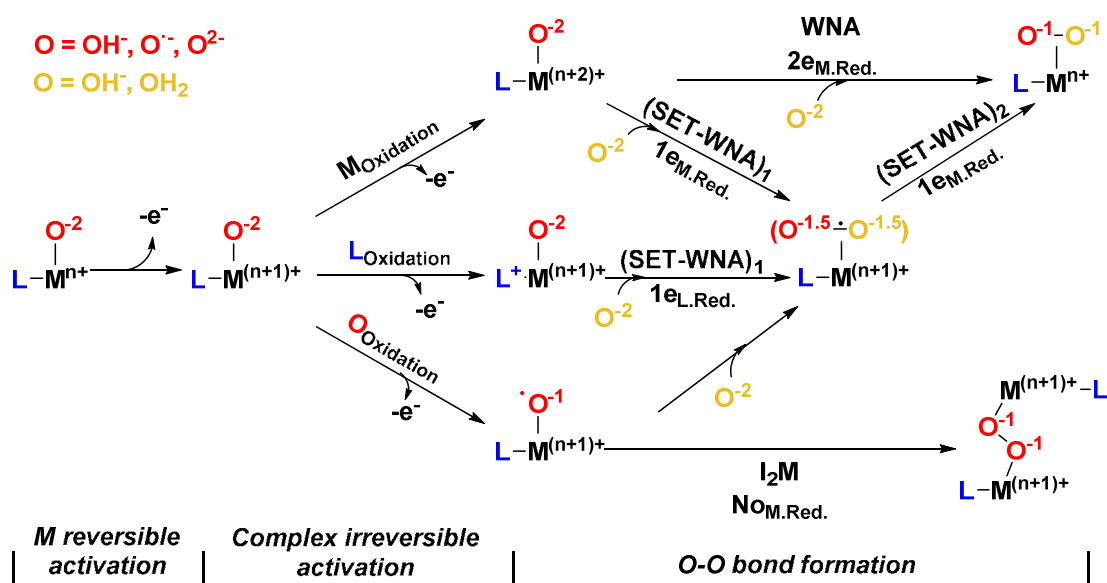**An overview of the new mechanistic scenario**

Figure 6. Overview of the water oxidation mechanisms. The oxygen directly attached to the metal is marked in red, the incoming oxygen is marked in yellow.

The results reported above make a strong case that SET-WNA has to be added to the list of mechanisms available for water oxidation. We make an effort in this section to put together all available mechanisms in a single view, summarized in Figure 6. The overall process consists of the abstraction of at least two electrons, either by chemical or electrochemical methods from a metal complex, and the absorption by this complex of two electrons from two oxygen centers (each in formal oxidation state -2) to make a peroxide bond (each oxygen atom in formal oxidation state -1).

The left part of Figure 6 deals with the electron abstraction from the complex. The reaction usually starts with the oxidation of the metal center in a reversible way. This step is shared by the four systems analyzed in this work, with the peculiarity that for the Ru the two electrons are mainly abstracted from the metal center. The next step involves the removal of an additional electron that can occur at three different sites within the complex: the metal center, the ancillary ligand or the oxygen ligand itself. In Ru complexes with neutral ligands such as $[(L3)(L4)Ru^{II}(H_2O)]^{2+}$ described above, the electron is mainly abstracted from the metal center. In the $[(L3)Cu^{II}(OH)_2]$ system, the second electron is removed from the oxygen ligand since the IV/III metal based redox potential for copper is very high. This produces the corresponding Cu(III)-oxyl species that is very active. Finally, the combination of a metal difficult to oxidize and a redox-active ligand leads an intermediate situation with a ligand-centered radical, as happens in $[(L1)Cu^{II}]^{2-}$ and $[(L2)Cu^{II}(OH_2)_2]$.

After the oxidation is completed, the system is ready for the O-O bond formation step. Again, three different mechanisms are available, water nucleophilic attack (WNA), single-electron transfer water nucleophilic attack (SET-WNA) and interaction of two M-O units (I2M) mechanism. The WNA mechanism is formally the simplest as it proceeds in one step through a

single transition state. A lone pair in the external oxygen attacks the metal-bound oxo center, which in turn transfers two electrons to the metal. As a result, the metal oxidation state is diminished by two units, and a single O-O bond is formed. The WNA mechanism requires thus a metal center in a high oxidation state, which can remove enough charge from the oxygen center to make it suitable for nucleophilic attack. This is most easily accomplished with second- or third- row transition metal centers, as is the case for the $[(L3)(L4)Ru^{II}(H_2O)]^{2+}$ discussed above. A second well-recognized mechanism is the I2M, which requires a relatively accessible oxyl species that are able to couple. Each oxygen atom is already oxidized to oxidation state -1 by the external oxidant and thus formally no metal reduction takes place. This mechanism requires stable oxyl radical complexes with low charges, as the two complexes need to come together. The additional mechanism we are proposing, SET-WNA, share similarities with the two previously described but has some specific features. In SET-WNA, the external oxygen does not transfer two electrons in a single step to the complex, but makes two single one electron transfers. The most significant difference between SET-WNA mechanism and the WNA and I2M just described is the formation of a (HO•••OH)- fragment, where there are two electrons in the σ O-O orbital and one in the σ* O-O, thus with a bond order of 0.5. We have shown in the examples above that it is operative for the three copper complexes studied.

   The SET-WNA mechanism completes the general scheme by connecting the two conventional mechanisms, as it may proceed in principle from either the $M^{(n+2)+}$oxo systems typical of WNA or from the $M^{(n+1)+}$oxyl systems typical of I2M. More significantly, SET-WNA depends critically on the stability of the $M^{(n+1)+}$ (HO•••OH)- intermediate, defining thus a new paradigm for catalyst optimization. The SET-WNA fits well with the characteristics of first row transition metals, and has been shown to operate with fast catalysts where the overpotential is easily

controlled. The introduction of this new mechanism will help experimental and computational chemists to design new efficient WOCs based on first row transition metals as well asexplore and characterize their low energy path-ways.

Computational Details

All calculations were performed using the DFT approach with the B3LYP-D3 functional,[48,49] and a basis set with diffusion and polarization functions in all atoms. Solvation was introduced implicitly with water as the solvent. The role of the introduction of a water molecule was evaluated (Figure S7) and found to be not necessary. All geometry optimizations were carried out in solution without symmetry restrictions. Unless otherwise mentioned, all reported energy values are free energies in solution. Full computational details are provided in the Supporting Information.

ASSOCIATED CONTENT

The supporting information includes extended computational details, additional mechanisms, and Cartesian coordinates of all structures reported. A dataset collection of computational results is available in the iochem-db database.[50] This material is available free of charge via the Internet at http://pubs.acs.org.

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ABBREVIATIONS

6,6'-dhbp= [2,2'-bipyridine]-6,6'-bis(olate),

bpy= 2,2'-bipyridine

OPBAN= o-phenylenebis-(oxamidate)

damp= 2,6-bis((dimethylamino)-methyl)pyridine

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