## **Review Article**

## **Progress on Homogeneous Ruthenium Complexes for Water Oxidation Catalysis: Experimental and Computational Insights**



## Ernest Opoku a, b,\*

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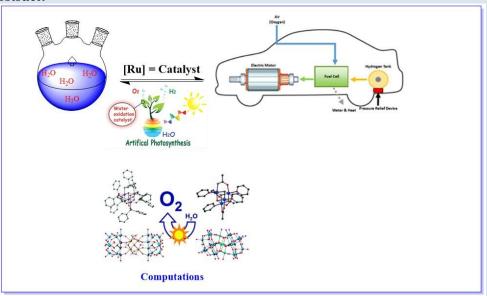
#### **Abstract:**

This work presents a concise review on the homogeneous ruthenium single-, two, and three-center complexes employed in water oxidation catalysis. The design of efficient and robust water oxidation catalysts has much to benefit from an improved understanding of the mechanism. A strong perspective is established on the progress made so far on the water oxidation catalysis through experimental and complementary computational efforts to understand the water oxidation reaction. The general mechanisms postulated so far are including the acid-base mechanism, the water nucleophilic attack and the direct coupling mechanistic approaches. These proposals are briefly discussed and reports featuring each instance are captured. From experimental perspectives, considerable efforts have been made in optimizing catalyst figures of merit (overpotentials, turnover numbers, and operating conditions) in single-center Ru systems, their efficiencies in most cases are not realistic enough to be adopted in commercial scale. While homogeneous multinuclear ruthenium complexes exist in the literature, few studies have been devoted towards understanding their mechanisms. Further studies in this respect are crucial as they may serve as the golden gate towards understanding (probably) the mechanisms involved in the nature's photosystem II which is the upper-bound catalyst for water oxidation. The present experimental and computational progress made in single- and twocenter homogeneous catalytic systems provide a useful blueprint to build on higher homologous series for efficient water oxidation catalysis.

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**Keywords:** Water oxidation; Catalysis; Water splitting; Ruthenium complexes; Hydrogen fuels; Homogeneous catalysis.

#### **Graphical Abstract:**



<sup>\*</sup>Corresponding author: Ernest Opoku, Email: <a href="mailto:ernopoku@gmail.com">ernopoku@gmail.com</a>



<sup>&</sup>lt;sup>a</sup> Theoretical and Computational Chemistry Laboratory, Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

<sup>&</sup>lt;sup>b</sup> Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849-5312, USA

## **Biography:**



**Ernest Opoku** received his B.Sc. (Hons) in Chemistry and M.Phil. Physical Chemistry degrees from the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. Presently, he is a Ph.D. student at the Auburn University, AL, USA. His research areas include catalysis, theoretical and computational chemistry.

## 1. Background to Water Oxidation Catalysis

The sunlight-driven splitting of water into molecular oxygen and hydrogen fuels (Equation 1 and 2) is a promising long-term source of carbon neutral and sustainable energy [1]. The construction of appropriate devices for water splitting requires the combination of several intricate chemical processes such as light harvesting, charge separation, electron transfer, water oxidation and reduction of the generated protons to the desired solar cell [2,3]. Presently, the major setback in this ultimate objective is the water oxidation step which is found to be thermodynamically uphill [4-6] (Equation 2).

$$2H+2e-\rightarrow H_2$$
  $E_0 = 0.00V \ vs \ NHE$  (1)

$$2H_2O \rightarrow 2H + 2e - + O_2$$
  $E_0 = 1.23V \text{ vs NHE}$  (2)

The complexity of the water oxidation reaction step is illustrated by the prohibitive over potentials associated with performing the reaction by means of any of the several stepwise approaches [7-9], as shown in Equations 3-5.

$$2H_2O \rightarrow 3H + + 3e - + HO_2$$
  $E_0 = 1.66V \text{ vs NHE}$  (3)

$$2H_2O \rightarrow 2H^+ + 2e^- + H_2O_2$$
  $E_o = 1.76V$  vs NHE (4)

$$H_2O \to H^+ + e^- + OH^*$$
  $E_0 = 2.72V \text{ vs NHE}$  (5)

Considering the stepwise mechanistic perspectives, it is likely that the optimal pathway for the water oxidation is a concerted mechanism [10]. Therefore, selective and efficient catalysts are required to carry out this reaction at accessible potentials using the photovoltaics that capture visible light [11].

In nature, the four-electron water oxidation reaction is catalyzed by a tetranuclear manganese ( $Mn_4$ ) cluster embedded within the oxygen evolving complex (OEC) of photosystem II [12–14]. This special metalloenzyme system catalyzes the water oxidation at rates and efficiencies that far exceed any synthetic catalyst [15]. Consequently, efforts have been made to resolve the structure of the OEC in plants using X-ray analysis [16], experimental [17] and computational [18] techniques. The overall objective is the ability to understand thoroughly, the reaction mechanism involved in the water oxidation reaction within the OEC. At this stage that understanding reaction mechanisms is a necessary requirement to gain total control over reactions and easily optimize and

influence product outcomes [19–24]. Therefore, understanding the reaction mechanisms involved in the water oxidation catalysis will provide theoretical guidance for correlative experiments [25,26]. From theoretical perspective, the essential steps of the water oxidation mechanisms can be studied rigorously and comprehensively by carefully focusing on much simpler synthetic catalysts, which do not have the extensive protein folding that often complicates efforts to understand the natural system [27,28].

Towards this end, several synthetic catalysts [3, 29– 31] for water oxidation have been synthesized and characterized, ranging from single-center metal clusters [32] to amorphous materials [33] and periodic metal oxide systems [34]. Among the families of synthetic catalysts, the single-center [35,36] metal complexes and dimers [37] have demonstrated that the catalyst performance may depend on the chemical and structural variations [38,39]. However, a systematic method for catalyst optimization remains elusive, prompting the need for mechanistic understanding [40]. Recent theoretical studies [41,42] on this subject have been very helpful in the effort to understand the water oxidation mechanism by providing highly detailed geometrical and energetic data at the molecular level.

In this paper, a thorough review (with key focus on mechanisms) of carefully selected articles on homogeneous single-, two-, and three-center homogeneous ruthenium complexes for water oxidation catalysis are presented. In first instance, extreme emphasis are placed on the acid-base mechanism [40] involved in the ruthenium water oxidation catalysis. Subsequent sections present on the direct coupling and the water-nucleophilic attack (WNA) mechanisms [28,43,44] of chosen single-, two- and three-center ruthenium complexes and discussed in light of recent progress and studies. The technique of metal-ligand cooperation, base and additives contributions towards developing efficient and active homogenous ruthenium water oxidation catalysts [45] are brought into perspective. The study highlights the synergistic experimental and quantum chemical approach in understanding metal-ligand cooperation in the catalysis of the water oxidation reaction [45–47]. In the final section, the summary on research progress on ruthenium water oxidation catalysis is captured. In addition, future directions and



recommendations for ruthenium water oxidation catalytic designs are brought into perspective.

## 2. General Mechanistic Proposals for Homogeneous Water Oxidation

Currently there are two dominant scenarios for the homogeneous water oxidation mechanism, known as the acid-base (AB) and direct coupling (DC), as shown in Figure 1 [40]. In the AB mechanistic picture, an oxygen nucleophile (*e.g.* water or hydroxide) attacks a metal-bound electrophilic oxo group. From orbital perspectives, a HOMO $\sigma$  orbital approaches the M-O  $\pi^*$  orbital (LUMO).

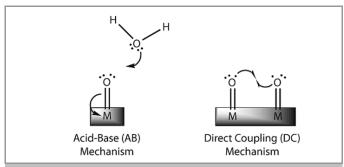


Figure 1. Schematic representations of acid-base and direct coupling pictures.  $M = Metal \ center \ [40].$ 

This orbital interaction leads to formation of an O-O σbond while breaking one of the M–O π bonds, representing a formal 2e<sup>-</sup> reduction of the metal center. The AB picture is widely thought to describe appropriately the O-O bond forming chemistry in the oxygen-evolving complex of photosystem II [48,49]. In the DC mechanistic picture, O-O bond formation occurs between two metal-bond radicaloidoxo groups [36]. Here the O-O bonding orbital arises from the combination of two single occupied orbital of M-O  $\pi^*$  character. Although there is no biological precedent for the DC mechanism, it has widely been implicated [50] to be the underlining mechanism in the design of two-center water oxidation catalysts. Many of the implicated two-center water oxidation catalysts use cofacial or conformationally locked geometries [51,52] to promote direct coupling. Tamaka et al. [53] have developed a two-center water oxidation catalysts (WOC) and found intermediates containing a direct O-O coupling [54]. This study has been supported by a subsequent DFT mechanistic studies Muckerman and co-workers [7]. Muckerman's study among other reports [46,55] provide interesting insights into the proposed catalyst intermediates; however, no energetics data were provided to assess the viability of the overall catalytic cycle.

Recently, the AB picture has received increasing attention in synthetic water-splitting catalytic designs [56,57]. The AB picture has been suggested by several

groups [58,59] to be the underlying mechanism at single-metal sites [60,61]. It ought to be mentioned that, some experimental studies involving single-center water oxidation catalysts in heterogeneous oxide surfaces [62] and in multicomponent [63] light-driven water oxidation systems provide further support for the viability of the AB picture [64]. Some studies [52,65,66] have begun on optimizing single center catalysts by systematic variation of electronic parameters of the ligands [67] in light of the AB mechanistic picture. Fan and co-workers [68] reported an exhaustive computational studies on the competitive AB and DC mechanistic routes in homogeneous ruthenium water oxidation catalysts.

Voorhis *et al.* [40] assessed the viability of the AB mechanism for WOC. This was done by conducting mechanistic investigations on selected single- and two-center ruthenium catalysts using DFT at the B3LYP level of theory. The Los Almos LANL2DZ was employed as the effective core potential for the metal centers. Subsequently, redox potentials for oxidative couples in the catalytic cycle using the polarizable continuum model for solvent effects are calculated and discussed. Their study [40] implicated the AB mechanism as the plausible route in single-center ruthenium complexes for water oxidation catalysis. Several studies have also found the AB mechanism plausible in ensuing articles [2,53,69,70].

## 3. Single-Center Ruthenium Catalysts

The mechanism of the water oxidation catalysis with the single-center catalyst,  $[Ru^{II}(tpy)(bpm)(OH_2)]^{2+}[40]$  in light of the AB picture has been investigated followed by recent studies of analogous molecular water oxidation catalysts [71–73]. The coordination geometry of the central Ru atom is pseudo-octahedral [74], and catalysis occur at the water bound site [75]. Kinetic studies [70] suggests the rate of water oxidation is first-order in the catalyst concentration, indicating that no more than one metal center is involved in the rate limiting step, and perhaps the entire catalytic step [76]. The complete mechanistic cycle including calculations on all reactants, products, intermediates, energetics and reaction barriers as reported by Voorhis *et al.* [40] are presented in Figure 2.

#### 3.1. Energetics and redox potentials

Four water oxidation events are required to produce a single oxygen molecule. Various intermediates in the catalytic cycle involved in the water oxidation are demonstrated in Figure 2, beginning with the aquo complexRu<sup>II</sup>(OH<sub>2</sub>), labeled as **0**.



$$\mathbf{4}_{(q=+2, S=1)}$$

$$\mathbf{4}_{($$

Figure 2. Complete catalytic cycle for the single-center water oxidation catalyst. Lowest-energy spin states are denoted in subscripts. Bracketed species are not experimentally observed. The Ru<sup>V</sup> species is sufficiently high in energy and unstable that we denote it using "2T", where "T" stands for "transient". Experimental values for redox potentials are reported in parentheses. [40]

Experimental measurements and their interpretation are as follows. A two-electron wave was observed at 1.20 V versus NHE, taking the aquo complex O directly to the oxo species Ru<sup>IV</sup>(O) (2). The hydroxospecies 1 is not experimentally observed, indicating that it disproportionates to 0 and 2; thus the redox potentials of the RuII/RuIII and RuIII/RuIV couples average out to 1.20 V, with the former being higher. Both oxidation events are pH-dependent proton-coupled electron transfer (PCET) steps [77]. At 1.65 V, a pH independent one-electron wave appears as a pre-feature of the catalytic wave and is assigned to the oxidation of 2 to Ru<sup>V</sup>(O) (2T). 2T contains the highly oxidized Ru<sup>V</sup>, which undergoes nucleophilic attack by a solvent water molecule, forming an oxygen-oxygen bond and losing a proton to create the hydroperoxo complex Ru<sup>III</sup>(OOH)(3). This complex is oxidized a fourth and final time to yield the peroxo complex Ru<sup>IV</sup>(OO) (4); this fourth couple has an unknown potential that is bounded from above by the catalytic wave. The peroxo complex 4 returns to the rest state **0** via displacement of the peroxo group by a solvent water molecule, releasing oxygen.

As seen in Figure 2, all the standard Gibbs free energies and the standard redox potentials for all the entire catalytic cycle are reported. In the case of the standard redox potential, the experimentally derived values are reported in parenthesis against the calculated ones in all steps. The calculated redox potentials for the  $Ru^{IV}/Ru^{V}$  couple ( $2\rightarrow 2T$ ) is very high at 1.98V which is where the redox complex was

observed by Meyer *et al.* [78]. At this step, a statistically significant discrepancy is observed between theory and experimentally obtained redox potentials. The authors speculated that the disagreement may stem from the fact that 2T is the only species in the entire cycle with the +3 charge. Alternatively, the oxidation of 2 at 1.65V may be achieved through an activated process but reaching 2T would require crossing an additional kinetic barrier. The calculated standard redox potential for the final redox couple ( $3\rightarrow4$ ) is 1.30V, below the experimental upper bound of 1.65V.

#### 3.2. Oxygen-oxygen bonding catalytic step

The O-O bonding step is the most chemically interesting step since it corresponds directly to the AB where water nucleophile attacks electrophilic metal oxo group. In preliminary calculations, the authors explored several mechanistic proposals. The authors found no O-O bonded structure involving Ru<sup>IV</sup>(O), suggesting that higher oxidation states are responsible for the O–O bonding. It was also found that any bimolecular O-O bonded structure Ru<sup>IV/V</sup> (O)–(O) Ru<sup>IV/V</sup> is at least 100 kcal/mol higher in energy than the two monomers. This observation is likely a consequence of electrostatic repulsion between these positively charged species. Therefore, the possibility of a bimolecular direct coupling is eliminated.

Subsequently, Voorhis *et al.* [40] evaluated addition of water to  $Ru^{V}(O)$  (2T $\rightarrow$ 4). The kinetics surrounding the water addition is influential in validating the



proposed mechanism. A total of 40 configurations of  $2 + 4H_2O$  were sampled, fully relaxed and then oxidized. After oxidation of  $2T + 4H_2O$  and subsequent relaxation, it was observed that 3 out of 40 configurations spontaneously underwent the reaction  $2T + 4H_2O \rightarrow 3 + 2H_2O + H_3O^+$ . These reactions followed by nucleophilic attack of a water molecule on the metal oxo group, forming an O–O bond, coupled with proton transfer (PT) to a neighboring water molecule. Mullikan charge analysis show clearly that a unit of positive charge is transferred to the solvent after PT (Figure 3).

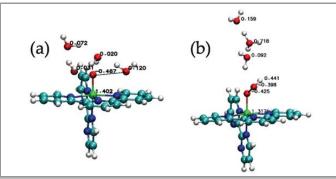


Figure 3. Starting and ending points of a geometry optimization starting at  $Ru^{\text{IV}}(O)$  and ending at  $Ru^{\text{III}}(OOH)$ .

Also, the calculations indicate that the O–O bonding thermodynamically step favorable  $(\Delta G =$ -6.5kcal/mol). Hence, the reaction pathway of the O-O bonding step  $(2T\rightarrow 3)$  is consistent with the AB picture for water oxidation. The authors also examined the bond lengths and molecular orbitals through the course of the O-O bonding to verify consistently with the AB mechanistic picture. It was found that, the oxidation of  $Ru^{IV}$  to  $Ru^{V}$  (2 $\rightarrow$ 2T) caused the Ru-O bond to shorten from 1.78 Å to 1.71 Å and reduced the Mulliken spin densities on Ru and O from 1.0/1.0 to 0.5/0.5. These observations concur with removing an electron from Ru-O  $\pi^*$  orbital and increasing the bond order to 2.5.

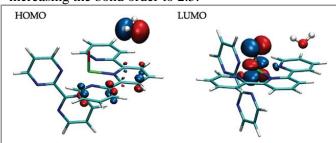


Figure 4. Isosurface plots of the HOMO and LUMO in 2T + H<sub>2</sub>O.

The nucleophilic attack of water and O–O bonding  $(2T\rightarrow 3)$  resulted in an O–O bond with length 1.37 Å, characteristic of a bond order of 1; the Ru–O bond order decreased as the bond lengthened from 1.71 Å to 1.94 Å. Hence, this also indicates consistency with the AB mechanism, for the O–O  $\sigma$  bonding orbital is

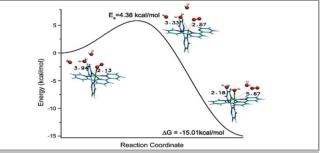
predicted to have Ru–O antibonding  $\pi^*$  character (Figure 4).

Figure 4 demonstrates that the water  $1b_1$  molecular orbital must be oriented towards the Ru–O axis for bonding to occur. This observation prompts the possibility to design catalysts which can coordinate nearby water molecules to facilitate this process.

#### 3.3. Dioxygen Replacement

The O–O bonding step leads the catalytic cycle to the hydroperoxo complex  $Ru^{III}$ –(OOH) (3). From this step, a fourth and final proton-coupled redox event takes the reaction to the peroxo complex  $Ru^{IV}$ (OO) (3 $\rightarrow$ 4). Upon thorough mechanistic investigations of this step, the results showed that the oxidation very likely follows a PCET pathway. The absence of a kinetic barrier for this step (3 $\rightarrow$ 4) predicts that 3 is not an observed intermediate which is in good agreement with experimental observations.

The authors also explored the reaction barrier for the oxygen displacement step  $4 + H_2O \rightarrow O + O_2$ . A triplet six-coordinate minima geometry was found for 4. The geometries and reaction coordinate for the dioxygen displacement step is shown in Figure 5. Following replacement of oxygen by water, the catalyst returns to the rest state (1) and the catalytic cycle is terminated.



**Figure 5.** Reaction diagram for oxygen displacement comparing the geometries and energetics of the starting, ending, and transition state configurations.

Recently, Aditi and Sumanta [79] reported a singlemononuclear complex tpy)(bpy)Cl]PF<sub>6</sub>(Ru-Cl) and its corresponding aqua  $[Ru(Fc-tpy)(bpy)OH_2](PF_6)_2(Ru-OH_2)$ complex complex (Fc-tpy = 4'-(2-ferrocenyl)-2,2':6'2"terpyridine) found to be an efficient water oxidation catalyst. They discovered that, under strong acidic conditions the Fe(II) center of the ferrocene moiety (Fc) undergoes protonation to generate Fe(IV) hydrido species Fe(IV)H (FcH<sup>+</sup>). The Ru aqua complex (Ru-OH<sub>2</sub>) complex shows one pKa value at 10.0 due to deprotonation of the aqua ligand. The Ru-OH2 complex was found to act as an efficient water oxidation catalyst at pH = 1.0 in triflic acid using cericammonium nitrate (CAN) as a sacrificial electron acceptor. The Ru-OH<sub>2</sub> complex exhibits a turnover number (TON) of **12**. whereas parent  $[Ru(tpy)(bpy)(OH_2)]^{2+}$ complex exhibits a TON of 10



under the similar conditions. The presence of ferrocenyl group coupled with terpyridine was concluded to have a potential to act as an electron donor and can stabilize the higher oxidation state of ruthenium complex required towards water oxidation. The rate of evolution of O<sub>2</sub>Ru-OH<sub>2</sub> is much higher compared with the parent [Ru(tpy)(bpy)- $(OH_2)$ ]<sup>2+</sup>complex with 230 mV of lower onset potential.

The authors [79] proposed the plausible catalytic cycle for the water oxidation process in the Ru-OH<sub>2</sub> follows the sequence  $[Fc^+-Ru^{II}-OH_2]^{3+} \rightarrow [Fc+ Ru^{V}=O^{4+} \rightarrow [Fc^{+}-Ru^{VI}=O]^{5+} \rightarrow [Fc^{+}-Ru^{IV}-O-OH]^{4+}$  $\rightarrow$  [Fc<sup>+</sup>-Ru<sup>V</sup>-O-O]<sup>4+</sup>  $\rightarrow$  [Fc<sup>+</sup>-Ru<sup>III</sup>OH<sub>2</sub>]<sup>4+</sup>  $\rightarrow$  [Fc<sup>+</sup>-Ru<sup>III</sup>-OH]3+as illustrated in Scheme 6 below. In an analogous report [80], a new mononuclear Ru aquo complex  $[Ru(C_8Otpy)(H_2dcbpy)(OH_2)]^{2+}$  with 4,4'dicarboxy-2,2'-bipyridine (H<sub>2</sub>dcbpy) and 4'-octyloxy-2,2':6',2"-terpyridine (C<sub>8</sub>Otpy) has also been found to efficiently catalase the water oxidation process.

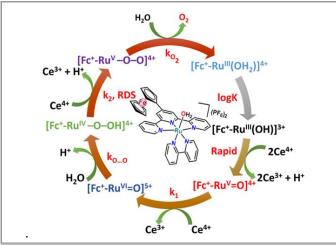
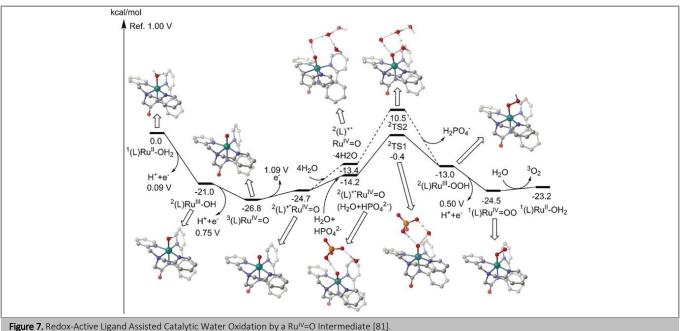
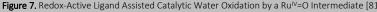


Figure 6. A plausible mechanism for water oxidation by Ru-OH<sub>2</sub> [79].

In other works, a new family of single-center ruthenium complexes [81,82] bearing oxidative electron-rich N<sup>5</sup>-ligand display impressive water oxidation performance with a lower overpotential (ca. 183 mV) in 0.1 m phosphate buffer (pH 7.0). It is the first Ru-based molecular catalyst which could initiate water oxidation with a Ru<sup>IV</sup>=O intermediate in neutral aqueous solution. Shi et al. [81] employed the DFT quantum chemical investigations on the catalytic system and the outcome are summarized in Scheme 7.  $[(L^{N5-})Ru^{III}-OH]^+$ is first oxidized [(L<sup>N5-</sup>)Ru<sup>IV</sup>=O]<sup>+</sup> by proton coupled electron transfer. The following ligand-centered oxidation significantly improved the reactivity of the [(LN5-)RuIV=O]+, and thus, the resulting [(LN5-)+RuIV=O]2+ could experience nucleophilic attack by water (WNA) to give an intermediate peroxide that could be further oxidized to release oxygen and close the cycle. For the WNA process, the presence of the HPO<sub>4</sub><sup>2-</sup> could lower the reaction barrier and benefit the O-O bond formation. The calculated barrier is overestimated comparing with the kinetics observation because the entropic contribution was significantly overestimated [83–87]. It is worth mentioning that, the oxidation of the ligand plays a crucial role in the initiation of the catalytic process with a Ru<sup>IV</sup>=O at pH 7.0. Vereshchuk et. al. [88] have also recently reported a new Ru complex containing the deprotonated 2,2':6',2"-terpyridine-6,6"-diphosphonic acid (H<sub>4</sub>tPa) and pyridine (py) of general formula  $[Ru^{II}(H_3tPa-\kappa-N_3O)(py)_2]^+$  whose chemistry is in good agreement with the water nucleophilic attack mechanism where the second coordination sphere of the ligand play a dominant role as noticed in several reports from the chemical literature [89–96].







### 4. Two-Center Ruthenium Complex Catalysts

Investigation of the water oxidation mechanism in two–center Ru catalyst is also actively ongoing by several groups [51,97–100]. Voorhis [40] investigated the water oxidation mechanism of the dibenzofuran (DBF) bridged two-center Ru<sup>II</sup> complex [(bpy)(H<sub>2</sub>O)Ru<sup>II</sup>(tpy-DBF-tpy)]Ru<sup>II</sup>(OH<sub>2</sub>)-(bpy)]<sup>4+</sup> (Figure 8).

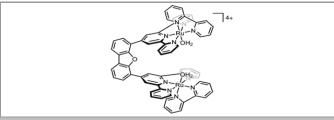


Figure 8. Dibenzofuran (DBF) bridged two-center ruthenium catalyst.

The DBF bridged two-center complex is found to proceed with the catalytic water oxidation through the acid base mechanism. The elementary catalytic steps involved are illustrated in Figure 9.

The initial state is the singly oxidized specie 5. Three proton-coupled redox events give rise to the  $[(O)Ru^{IV}Ru^{IV}(O)]^{4+}$ state (6), containing ruthenium oxo groups. A fourth redox event yields the Ru<sup>V</sup>-containing high-energy intermediate  $[(O)Ru^{IV}Ru^{V}(O)]^{5+}$ (**6T**). **6T** undergoes nucleophilic attack and deprotonates to give [(O)Ru<sup>IV</sup>-Ru<sup>III</sup>(OOH)]<sup>4+</sup> (7). There is a remarkable similarity between the O-O bond forming step in the single center  $(2\rightarrow[2T]\rightarrow3)$ . The Ru<sup>II</sup>(OOH) group in 7 is deprotonated via an intramolecular PCET, resulting in a peroxo species [(HO)Ru<sup>II</sup>-Ru<sup>IV</sup>(OO)]<sup>4+</sup> (8).

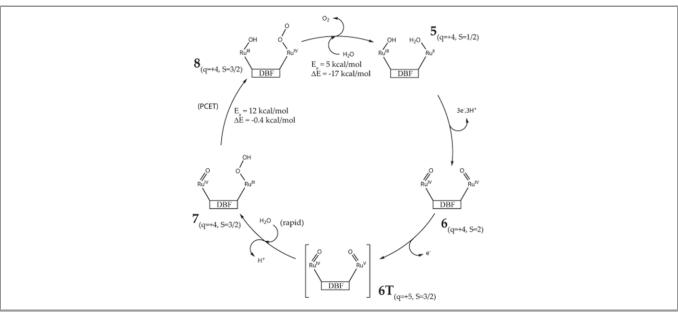


Figure 9. Proposed catalytic mechanism for the DBF-bridged two-center catalyst [40]

The Ru<sup>IV</sup>(OO) peroxo is replaced by water in a substitution reaction to yield **5**, releasing dioxygen and completing the catalytic cycle. The O–O bond formation, deprotonation of the hydroperoxo group and the dioxygen release steps were found to proceed in a similar catalytic fashion as evident in the single-site Ru catalyst and other reports [101,102].

It must be noted that the authors did not investigate the sequential pathways by which proton transfer (PT) and electron transfer (ET) may occur. However, they speculated that if a concerted pathway is assumed, barrier heights could be estimated using the driving force ( $\Delta G$ ) and reorganization energies. This was done within the framework of the Marcus theory formula  $Ea = \Delta G + \lambda)^2/4\lambda$ . Figure 10 illustrates the energetic relationships using a single combined PT and ET coordinate. They found a small  $\Delta G = -0.4kcal/mol$  for reactants and products;  $\lambda_R = 50.9$  kcal/mol and  $\lambda_p = 10.00$ 

46.1 kcal/mol. They chose to use the average of the  $\lambda$  values which yields activation energy of 11.9kcal/mol.

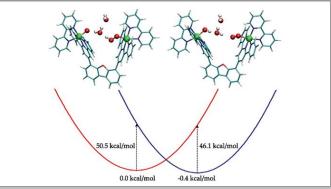


Figure 10. Marcus energy diagram showing the reactant  $[(O)Ru^{IV}Ru^{II}(OOH)]^{4+}$  and product  $[(HO)Ru^{III}Ru^{IV}(OO)]^{4+}$  configurations in the final PCET step [40].

## 5. Trinuclear ruthenium complex catalysts for water oxidation catalysis



In addition to several mono- and two-center water oxidation catalysts that are synthesized and their chemistry well studied, there are also some studies conducted on the trinuclear ruthenium complexes. It has been demonstrated in recent times that highly active water oxidation catalysts can be generated by incorporation of the catalytically active Ru(bda) metallosupramolecular complex fragment into macrocycles [14,42]. Kunz *et al.* [103] have synthesized series of trinuclearmetalloa supramolecular Ru(bda) macrocycles and the impact of the ring size on the catalytic activity in homogeneous water oxidation has been elucidated (bda = 2,2'-bipyridine-6,6'-dicarboxylate). Kinetic studies and <sup>18</sup>O labelling experiments suggested that these metallosupramolecular catalysts operate via the water nucleophilic attack (WNA) mechanism in which highly oxidized Ru<sup>V</sup>=O species are nucleophilically attacked by water molecules [104-106]. To obtain further insights into the different molecular properties, the authors employed molecular dynamics simulations using a QM/MM approach for all reaction steps as seen elsewhere [107,108], revealing that the size of the cavity strongly influences the hydrogen-bonded water network inside the macrocyclic structure and thus, important proton-coupled reaction steps of the catalytic cycle. For the most active catalysts, all reactive sites point into the interior of the cavity, which is supported by a single crystal X-ray analysis of the largest macrocycle, and a cooperative effect between the individual Ru(bda) centers facilitating proton abstraction has been substantiated. On the hand, different structural conformations predominate the smaller macrocycles, which prevent efficient interactions between the Ru(bda) centers.

## 6. Metal-ligand cooperation in single-site ruthenium water oxidation catalysts

Cramer and his co-workers [43] and other studies [109,110] have reasoned that complexes containing two Ru-OH<sub>2</sub> bonds are of special interest in water oxidation catalysis since they can potentially lose  $4H^{+}/4e^{-}$ . quality found in This is cis- $[Ru^{II}(bpy)_2(H_2O)_2]^{2+}$ (*cis-*1) and other similar complexes [38]. Toward this end, M06-L DFT and CAS SCF/CASPT2 calculations were carried out to better characterize the electronic structure of the formally bis-oxoRu<sup>VI</sup> state derived from cis-1 (Equation 6) and its implications for water oxidation reactivity. DFT calculations have also been reported on other ruthenium systems in the same family [111].

$$Cis$$
-[Ru<sup>II</sup>(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>+4H<sup>+</sup>+4e<sup>-</sup> $\rightarrow Cis$ -[Ru<sup>VI</sup>(bpy)<sub>2</sub>(O)<sub>2</sub>]<sup>2+</sup>
(6)

Analysis of the molecular orbitals (MOs) obtained from both M06-L DFT and CAS SCF/CASPT2 levels

of theory (Figure 11) suggests that the supported RuO<sub>2</sub> subsystem involves substantial covalency between the Ru and O atoms. The RuO<sub>2</sub> subsystem includes a three-center-six-electron fragment, similar to an organic ally moiety (except that Ru contributes two atomic d orbitals to the hybrid MOs instead of the atomic p orbital).

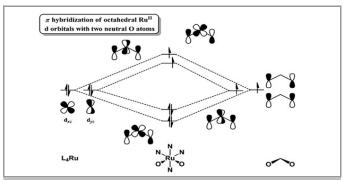
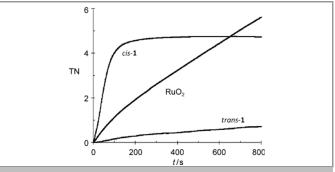


Figure 11. Hybridization of Ru d and O p orbitals resulting in net one electron oxidation of  $Ru^{\parallel}$  [43].

Therefore, the formed Ru<sup>II</sup> atom with six 4d electrons has two such electrons that by symmetry contribute only one to Ru–O  $\sigma$  bonds, and four 4d electrons in the  $\pi$  system; the two O atoms each contribute one 2p electron to the  $\pi$  system. The other five electrons on each O atom comprise two lone pairs and half on a Ru–O  $\sigma$  bond. Hence the resulting hybridization of the  $\pi$  MOs leads to a narrow separation between the two highest energy orbitals (as shown in Figure 8) so that the singlet and triplet states are close to one another in energy (the singlet is preferred by 3.9 and 4.6 kcal/mol). Vibrational spectroscopy analysis has also been used to locate the oxygen binding motif in some studies [112].

## 6.1. Reactivity of cis-[Ru<sup>II</sup>(bpy)<sub>2</sub>(H<sub>2</sub>O)]<sup>2+</sup>toward O<sub>2</sub> evolution reaction

Water oxidation with O<sub>2</sub> evolution by *Cis-1* was originally thought by experimentalists to proceed *via* an *in situ* generation of RuO<sub>2</sub> as the active catalytic specie [113]. However, Cramer *et al.* [43] demonstrated (Figure 12) that, the *cis-1* is capable of catalytically producing dioxygen at a much faster rate than either RuO<sub>2</sub> or *trans-1* (Figure 12).

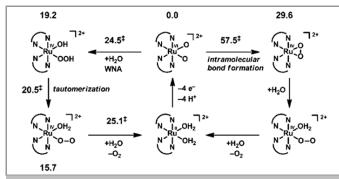


**Figure 12.**  $O_2$ -evolution profiles (TN=turnover number) for *cis*-1, *trans*-1, and  $RuO_2$  [43].



## 6.2. Mechanism of Cis-1 water oxidation catalysis derived from experiments and computations

Cramer *et al.* [43] conducted <sup>18</sup>O-labelling experiments for the *cis-***1** water oxidation and found unambiguously that the only plausible mechanism proceed through the water nucleophilic attack (WNA) as depicted in the left catalytic cycle in Figure 13. Synthetic strategies for manipulating the rate-limiting step have also been found in the literature [11].



**Figure 13.** M06-L free energies (kcal/mol) including SMD aqueous solvation for WNA (left cycle) and intramolecular bond formation (right cycle) [43].

The experimentally established WNA mechanism was complemented by results from computational calculations. As seen in Figure 13, the activation free energies for WNA (left of cycle) and intramolecular O–O bond closure (right of cycle) differ by 32.4 kcal/mol with the latter being strongly disfavored. The remaining steps in the WNA pathway were also characterized and found to proceed with roughly similar activation free energies relative to the initial reactant [Ru<sup>II</sup>(bpy)<sub>2</sub>(O<sup>-0.5</sup>)<sub>2</sub>]<sup>2+</sup> (Figure 13). Catalytic water oxidation by Ruthenium complexes containing negatively charged ligand frameworks are also known [47].

In brief, through the isotopic labelling experiments and the complementary computational calculations, Cis-1 has been established as an active water oxidation catalyst and do so through the water nucleophilic attack. This work was the first example of a direct experimental and computational evidence for the WNA mechanism. These results were found to be in good agreement with the works of Voorhis and co-workers [40] and others [114] as discussed in a previous section. The rationale and systematic development of new homogeneous ruthenium complexes which involve the incorporation of multiple types of ligands [111] towards catalytic efficiency is now an actively ongoing research approach in the domain of molecular water oxidation catalysis. The use of proximal bases and other additives to promote the homogeneous water oxidation catalysis is also a common practice now [115].

# 7. Synergistic experimental and quantum chemical approach in understanding metal-ligand cooperation in the catalysis of the water oxidation reaction

Karkas and his co-workers [45] have reported that two Ru<sup>III</sup> complexes, [(H<sub>3</sub>hpc)Ru(pic)<sub>3</sub>]<sup>+</sup> (1) and [(Hhpb)Ru(pic)<sub>3</sub>]<sup>+</sup> (2) (Hhpbc=2-(2-hydroxyphenyl)-1H-benzo[d]imidazole-7-carboxylic acid; H<sub>3</sub>hpc=2-(2-hydroxyphenol-1H-benzo[d]imidazole-7-ol; pic = 4-methylpyridine) are capable of oxidizing water (Figure 14), both chemically and photochemically using [Ru(bpy)<sub>3</sub>]<sup>3+</sup>-type oxidants. From kinetic studies, it was found that the rates of O<sub>2</sub> evolution displayed a first-order dependency with respect to the concentrations of both catalyst 1 and 2 (Figure 14). The results suggest that O–O bond formation in these catalysts (1 and 2) occur at the single metal centers.

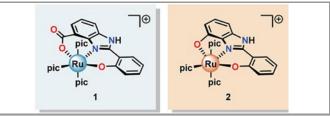


Figure 14. Molecular structures of complexes 1 and 2. pic=4-picoline.

## 7.1. Ligand exchange: generation of the catalytically active species

For WOCs to become catalytically active, it is necessary to have a free coordination site for an aqua ligand. The picoline—aqua ligand exchange enables PCET events, avoiding the formation of high-energy intermediates and effectively minimizing the energy required for carrying out multielectronchemistry. For Ru complexes 1 and 2, the ligand displacement reaction could theoretically occur at two positions, the equatorial (Equaion 10) or the axial position (Equation 11), as depicted in Figure 15.

 $[(L)Ru(pic)_{3}]^{+} + H_{2}O \rightarrow [(L)Ru(pic)_{2}^{ax}(OH_{2})^{eq}] + pic$  (10)

 $[(L)Ru(pic)_3]^+ + H_2O {\longrightarrow} [(L)Ru(pic)^{ax}(pic)^{eq}OH_2)^{ax}] + pic \ (11)$ 

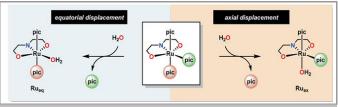


Figure 15. Pathways leading to the two isomeric aqua complexes Rueg and Ruax..

Previous studies [116] suggested that the ligand displacement for Ru complex 1 occurred at the equatorial position, resulting in species 1-Ru<sup>III</sup> (Figure 16). The conversion of Ru complex 2 to the corresponding aqua species was therefore examined by MS and <sup>1</sup>H NMR and got established that the



ligand displacement takes place at the equatorial position also for Ru complex 2 to provide species 2-Ru<sup>III</sup> (Figure 16).

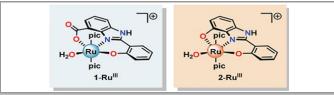
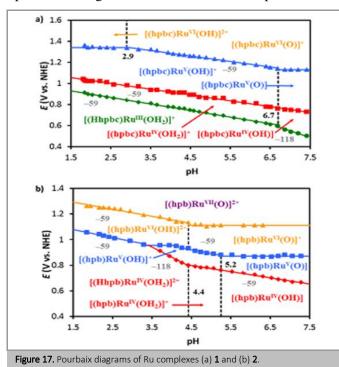


Figure 16. Structures of aqua complexes 1-Ru<sup>III</sup> and 2-Ru<sup>III</sup>

## 7.2. Electrochemical Insight into Catalytic Intermediates

To obtain further insight into the catalytic properties of the two single-site Ru complexes 1 and 2, electrochemical measurements were conducted, and the results discussed. Pourbaix diagrams were also constructed since they point out possible stable oxidation states and provide insight into the catalytic key intermediates. Figure 17 depicts the Pourbaix diagrams of complexes 1 and 2 in the range 1.5 < pH < 7.5. For Ru complex 1, three pH dependent redox processes were found before O<sub>2</sub> evolution was triggered, acknowledging that all redox processes are coupled to the removal of protons (Figure 17a). According to the previous work [116], the first process belongs to the Ru<sup>IV</sup>/Ru<sup>III</sup>redox couple.



## 7.3. Quantum chemical description of the various redox intermediates

A thorough computational calculations has been conducted to understand the mechanisms of the

complexes 1 and 2 catalytic activity towards water oxidation. The computational studies were conducted at neutral pH since the catalytic experiments were carried out under these conditions. Here, focus is centered on presenting the similarities and differences between Ru complexes 1 and 2. The calculations showed that at pH 7 both Ru-aqua complexes have a total charge of +1 in their Ru<sup>III</sup> state, labeled as 1-Ru<sup>III</sup> and 2-Ru<sup>III</sup>, respectively, where spin delocalization on the ligand scaffolds is evident.

According to the calculated Pourbaix diagram (Figure 17), a PCET oxidation leads to the formation of 2-Ru<sup>IV</sup>, in which the proton is released from the aqua ligand bound to the metal center and the electron is removed mainly from the ligands.

#### 7.4. Reaction mechanism

After establishing the key redox states involved for Ru complexes 1 and 2, calculations were subsequently performed to reveal possible mechanistic scenarios for generation of the O-O bond. Kinetic studies and the MS measurements suggested that generation of O<sub>2</sub> for Ru complexes 1 and 2 occurs at a single metal center. A likely reaction pathway for O–O bond formation for complexes 1 and 2 was computationally established to proceed via water nucleophilic attack on a highly oxidized Ru-oxo species to generate a hydroperoxo species-a mechanism which has been established for a plethora of Ru-based WOCs as discussed in earlier sections of this term paper. The overall catalytic cycle for complexes 1 and 2 were summarized (Figure 18).

For Ru complex 1, the reaction scenario involves water nucleophilic attack on a RuVI species to furnish hydroperoxo intermediate, which subsequently oxidized to a RuV-OO species that liberates  $O_2$  and regenerates the  $Ru^{\bar{I}II}$  catalyst. However, the O-O bond formation in complex 2 instead proceeds through a formal RuVII species, which is better described as having a Ru<sup>V</sup> center with a two-electron oxidized ligand framework. During the O-O forming event, two electrons are transferred to the ligand framework instead of the metal center as in complex 1. The rare nature of reaching such highvalent redox states originates from metal-ligand cooperation, a feature that is prevalent in Ru complexes 1 and 2, and certainly contributes to the observed catalytic activity. The results provided detailed insight into activation of water or related small molecules at a single metal center through nontraditional catalytic platforms [64].



Figure 18. Overview of the Proposed Catalytic Cycles for Ru Complexes 1 and 2.

#### 8. Conclusion

In this work, a review of carefully selected studies on homogeneous ruthenium single-, two-, and threecenter complexes were presented. The design of efficient and robust water oxidation catalysts has much to benefit from an improved understanding of the mechanism. It is now obvious from the review that much success has been achieved through experimental computational complementary efforts understand the water oxidation catalysis. A survey of the chemical literature revealed that, quite a few single-center homogeneous metal complexes based on Fe, Ir, Ni, and Pd have been synthesized. In some instances, considerable efforts have been made to understand their mechanisms. There is still some active research in single-center catalytic design to explore how optimizing the ligands may cooperatively enhance the catalysts performance.

There are few two-center systems that are capable of water oxidation found in the literature; however, the synthesis of these catalysts are highly difficult, and a strategy for optimizing catalyst figures of merit (overpotentials, turnover numbers, and operating conditions) remains elusive. Similar difficulties exist with increasing number of metal centers (trinuclear ruthenium complexes and higher homologous series). So far, very few computational reports are available on two-center complexes and higher homologous series. The obvious reason is the computational cost associated with such complexes. However, much effort still needs to be made to complement experimental gains.

Although, considerable amount of work has been done in optimizing catalyst figures of merit (overpotentials, turnover numbers, and operating conditions) in singlecenter Ru systems, their efficiencies are most cases not realistic enough to be adopted in commercial scale. Such a challenge prompts further efforts in much detail, tri- and tetra-nuclear metal complexes and perhaps ensuing complexes that are pretty much close to the photosystem II structure that may hold better catalytic performance. The present progress with single- two-, and three-center systems will be an excellent guide to build on higher homologous series.

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## **Disclosure statement**

The author declares that there is no conflict of interests whatsoever regarding this manuscript.

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