

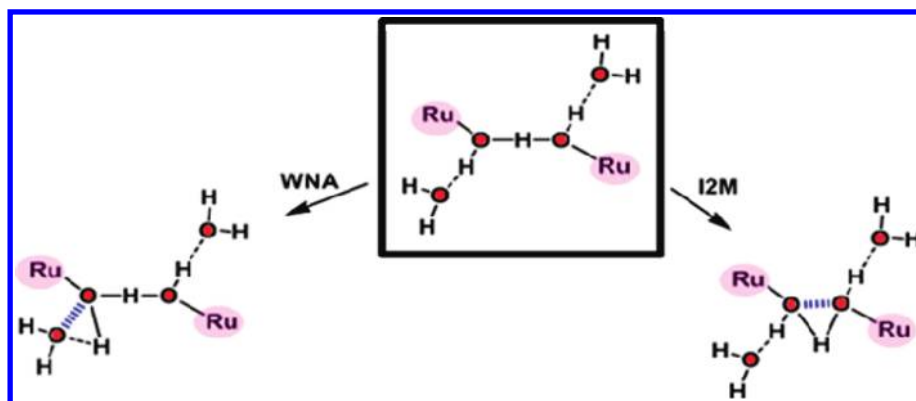
Oxygen–Oxygen Bond Formation Pathways Promoted by Ruthenium Complexes

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CONSPECTUS



The photoproduction of hydrogen from water and sunlight represents an attractive means of artificial energy conversion for a world still largely dependent on fossil fuels. A practical technology for producing sun-derived hydrogen remains an unachieved goal, however, and is dependent on developing a better understanding of the key reaction, the oxidation of water to dioxygen. The molecular complexity of this process is such that sophisticated transition metal complexes, which can access low-energy reaction pathways, are considered essential as catalysts. Complexes based on Mn, Co, Ir, and Ru have been described recently; a variety of ligands and nuclearities that comprise many complex topologies have been developed, but very few of them have been studied from a mechanistic perspective. One step in particular needs to be understood and better characterized for the transition-metal-catalyzed oxidation of water to dioxygen, namely, the circumstances under which the formation of O–O bonds can occur. Although there is a large body of work related to the formation of C–C bonds promoted by metal complexes, the analogous literature for O–O bond formation is practically nonexistent and just beginning to emerge.

In this Account, we describe the sparse literature existing on this topic, focusing on the Ru-aqua complexes. These complexes are capable of reaching high oxidation states as a result of the sequential and simultaneous loss of protons and electrons. A solvent water molecule may or may not participate in the formation of the O–O bond; accordingly, the two main pathways are named (i) solvent water nucleophilic attack (WNA) and (ii) interaction of two M–O units (I2M).

Most of the complexes described belong to the WNA class, including a variety of mononuclear and polynuclear complexes containing one or several Ru–O units. A common feature of these complexes is the generation of formal oxidation states as high as Ru(V) and Ru(VI), which render the oxygen atom of the Ru–O group highly electrophilic. On the other hand, only one symmetric dinuclear complex that undergoes an intramolecular O–O bond formation step has been described for the I2M class; it has a formal oxidation state of Ru(IV). A special section is devoted to Ru–OH₂ complexes that contain redox active ligands, such as the chelating quinone. These ligands are capable of undergoing reversible redox processes and thus generate a complex but fascinating electron-transfer process between the metal and the ligand.

Despite the intrinsic experimental difficulties in determining reaction mechanisms, progress with these Ru complexes is now beginning to be reported. An understanding of recent successes, as well as pitfalls, is essential in the search for a practical water oxidation catalyst.

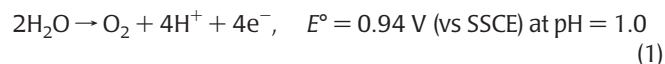
1. Introduction

The oxidation of water to molecular dioxygen is a reaction that takes place in the dark at the OEC-PSII.¹ It is a very interesting reaction to be modeled from a bioinorganic perspective to gain insight into the mechanism that operates in this natural system. It is of still greater importance from an energetic perspective, since water oxidation is recognized as the bottleneck for the development of commercial light harvesting devices for the photoproduction of H₂ from water.²

Water oxidation is a challenging task for a catalyst due to the large endothermicity of the reaction and to the large molecular complexity involved from a mechanistic point of view. During the last couple of years, there have been important developments with respect to the design of new transition metal complexes, characterized by different ligand sets and architectures that evolve dioxygen from water in the presence of an excess of a strong oxidant. This set of water oxidation catalysts allows grasping the tip of the iceberg of the variety of strategies that can be used to achieve this goal as well as the numerous problems associated with this catalytic process.² A fundamental piece of knowledge that is needed, to further develop this field to design efficient and rugged catalysts, is the understanding of the reaction mechanism through which this reaction can proceed promoted by transition metal complexes. Therefore, there is an urgent need to characterize reactive intermediates as well as decomposition pathways to avoid them. There are several issues that make mechanistic determinations challenging and that have been hampering its development. One is the intrinsic complexity of the reaction, where the catalyst is likely to cycle among five different oxidation states whether metal or ligand based or both.³ This imposes a requirement for transition metal complexes that need to be sufficiently long-lived to be able to perform the reaction and also to be spectroscopically detectable. Another fundamental problem is the unavoidable use of water as solvent, which is a problematic issue due to the limited temperature range at which reactions can be studied and due to its high absorptivity. One more problem associated with this reaction is the limited solubility of the catalysts or catalyst precursors in water. Furthermore, the high thermodynamic redox potential needed for water oxidation permits the catalyst to oxidize a broad range of organic and inorganic substrates, and thus, the presence of organic solvents can lead to undesired deactivation pathways.⁴

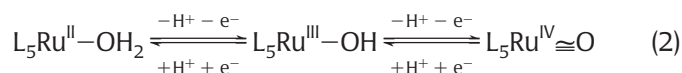
2. O–O Bond Formation Pathways Promoted by Ru Complexes

The oxidation of water leads to a range of species depending on the number of electrons removed whose thermodynamics are summarized in Table 1, together with interesting features of the oxidized species. As it can be observed in the table, the more electrons transferred, the lower the thermodynamic potential. Thus, a 1e[−] oxidation process has a prohibitive thermodynamic barrier of 2.5 V versus SSCE at pH = 1.0, whereas the four electron transfer (ET), as it happens at the OEC-PSII,⁵ has the lowest one,



This lowering of thermodynamics contrasts with the increase of molecular complexity. In the 4e[−] process, four O–H bonds from two water molecules have to be broken and an O–O bond has to be formed. Thus, the potential transition metal complexes that can be considered as candidates to carry out this reaction in a catalytic manner are required to deal with multiple ET process accompanied also with proton transfer management.

These requirements are met by Ru–OH₂ polypyridyl complexes discovered by Meyer's group about three decades ago.⁶ The capacity of Ru-aquo polypyridyl complexes to lose protons and electrons and easily reach higher oxidation states is exemplified in the following equation (L₅ = polypyridylic ligand)



The higher oxidation states are accessible within a narrow potential range mainly because of the σ–π-donation character of the oxo group. From a mechanistic perspective, the simultaneous loss of protons and electrons precludes an otherwise highly destabilized scenario with highly charged species. A proton-coupled electron transfer (PCET) type of process provides energetically reasonable reaction pathways that avoid high energy intermediates. For instance, for the disproportionation reaction of [LRu^{II}–OH₂]²⁺ (L = (bpy)₂(py); bpy is 2,2'-bipyridine and py is pyridine; see Scheme 1 for drawings and abbreviations of all the ligands discussed in this paper) and [LRu^{IV}≡O]²⁺ to give two molecules of [LRu^{III}–OH]²⁺, the energy penalty for a stepwise process with regard to the PCET is higher than 12.6 kcal/mol for the ET-PT and higher than 13.6 kcal/mol for the PT-ET whereas the concerted pathway is downhill by −2.5 kcal/mol. Furthermore, the energy of activation for the concerted proton–electron transfer process

TABLE 1. E° Values for the Oxidation of Water at pH 1.0 and 7.0 Together with Key Features of the Water Oxidized Species^a

| Redox couple | E° , V (vs. SSCE) | | H_2O Oxidized Species | | | |
|---|--------------------------|----------|---------------------------------------|----------------|-------------------|-------------------|
| | pH = 1.0 | pH = 7.0 | BO ^b | N ^c | Freq ^d | Dist ^e |
| $\cdot\text{OH} + 1\text{H}^+ + 1\text{e}^- \rightarrow \text{H}_2\text{O}$ | 2.50 | 2.15 | | | | |
| $\text{HO}\cdot\text{OH} + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ | 1.48 | 1.13 | 1 | 0 | 740-850 | 1.49 |
| $\text{HO}\cdot\text{O}\cdot + 3\text{H}^+ + 3\text{e}^- \rightarrow 2\text{H}_2\text{O}$ | 1.37 | 1.02 | 1.5 | 1 | 1100-1150 | 1.28 |
| $\text{O}=\text{O} + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ | 0.94 | 0.58 | 2 | 2 | 1560 | 1.21 |

^a The formal oxidation states of O-atoms are labeled according to the following code: -2, orange; -1, cyan; 0, green. ^b BO: O–O bond order. ^c N is the number of unpaired electrons. ^d Freq is the range of vibrational frequencies for the O–O bond in cm^{-1} . ^e Dist refers to the range of O–O bond distance in Å.

EPT is 10.1 kcal/mol and is lower than the thermodynamic value of any of the stepwise pathways.⁷

For purposes of simplicity and keeping track, with electron counting, formal oxidation states will be used in the present Account for the redox active atoms. Thus, as indicated in Table 1, oxygen atoms in oxidation state -2 are labeled in orange, -1 in cyan, and 0 in green. For the same reason, the oxidation states of Ru will be considered formally keeping in mind that electron distribution will depend on the rest of the auxiliary ligands. As an example, the complete bond description will be represented as a combination of two extreme resonance forms such as $\text{Ru(IV)=O} \leftrightarrow \text{Ru(III)-O}\cdot$.

Formally, from a mechanistic perspective, the formation of an oxygen–oxygen bond promoted by transition metal complexes can be classified taking into account whether an unbound free water molecule participates in the formation of the aforementioned bond. From this perspective, two possibilities exist:

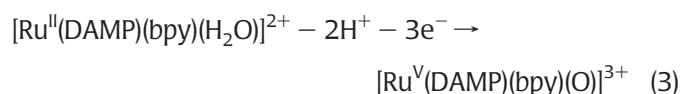
(A) Solvent water nucleophilic attack (WNA) to a M–O as depicted in Scheme 2. As written in the scheme, there is a 4ET demand which is quite a stringent demand for a mononuclear complex. A solution to that is to share the burden with more metal centers provided there is a bridging ligand (BL) that couples them electronically and thus allows generating a cooperative effect. Another option for a metal complex is to cycle up and down in similar oxidation states of different species as will be shown in the following section. It is interesting to point out here that the WNA is one of the favored mechanisms nowadays for the OEC-PSII⁸ and it is also the mechanism proposed for the inverse reaction, the reduction of dioxygen in the HIP Cyt-P450.⁹ Furthermore, the existence of this mechanism has been recently shown to occur in a Mn–porphyrin model complex.¹⁰ As it will be discussed in the following section, the nature of the complex can be mononuclear or polynuclear and it can have one or several Ru–O groups. In the

case of the latter, the job of each Ru–O group will be radically different. While one of them will be responsible for the O–O formation bond, the other(s) centers will be responsible for facilitating electron trafficking so that the 4e^- acceptance process can be shared among the different metal centers.

(B) The interaction of two M–O entities (I2M), displayed in Scheme 2. In the scheme, this reaction is described as a reductive elimination, but depending on the oxidation states of both the metal center and the oxygen atoms the O–O bond forming step could also be a radical–radical coupling reaction. As in the previous mechanism, here the nuclearity of the complex can also be variable.

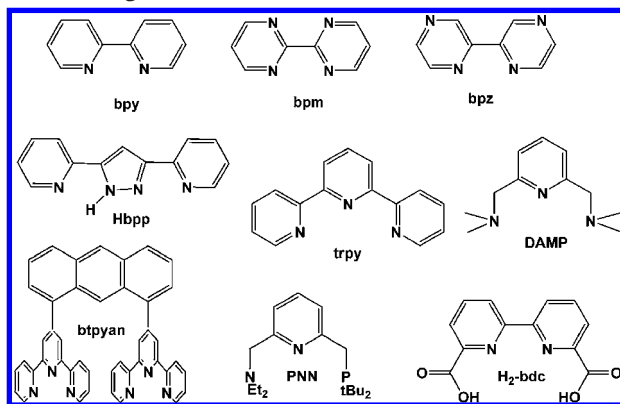
3. Water Nucleophilic Attack

3.1. Mononuclear Complexes. 3.1.1. The $[\text{Ru}^{\text{II}}(\text{DAMP})(\text{bpy})(\text{H}_2\text{O})]^{2+}$ Complex. More than 10 years ago, Thorp et al. reported the crystal structure of the complex $[\text{Ru}^{\text{IV}}(\text{DAMP})(\text{bpy})(\text{O})]^{2+}$ (DAMP is 2,6-bis(dimethylaminomethyl)pyridine), obtained by oxidation of the corresponding $\text{Ru}^{\text{II}}\text{-OH}_2$ complex.¹¹ The high stability of the $\text{Ru}^{\text{IV}}=\text{O}$ unit is due to the σ -donating nature of the tertiary amines of the DAMP ligand together with the extensive hydrogen bonding between the alkyl H atoms and the oxo group. We have recently shown that the combination of these ligand effects allows to reach even higher oxidation states and that the corresponding Ru^{V} is stable for a few minutes.¹²

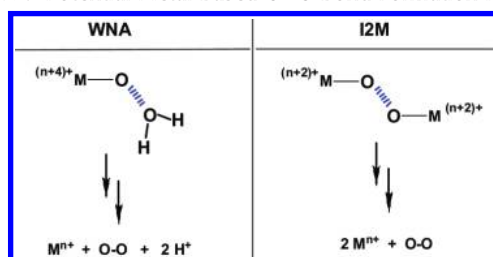


Further addition of one more oxidative equivalent of Ce(IV) produces dioxygen, and under excess Ce(IV) produces a handful of turnovers. Mass spectroscopic analysis using ^{18}O labeled H_2O and/or catalyst clearly indicates that in this case the reaction pathway is a WNA.

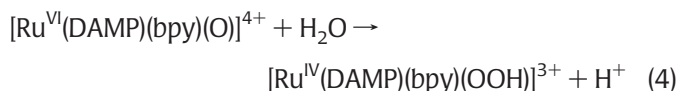
SCHEME 1. Ligands



SCHEME 2. Potential Metal Based O–O Bond Formation Pathways



With this information in hand, we are proposing a two oxidation step of the metal center that when reaches the formal Ru(VI) oxidation state suffers a water nucleophilic attack as shown in the following equation, generating a peroxidic intermediate

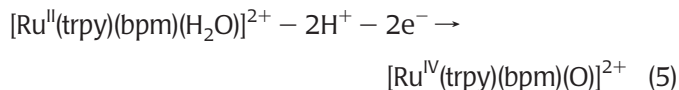


that undergoes further ET to form the initial Ru^{II}–OH₂ complex and dioxygen. The whole mechanistic proposal is shown in Figure 1 (left). A plot of the formal oxidation state of Ru versus the species generated along the reaction coordinate is presented in Figure 1 (right). In this case, the Ru complex initiates as Ru(II) progressively increases to Ru(VI) and then falls to Ru(II) again. As it can be observed in the figure, this graph resembles a volcano, and thus, it will be termed herein as “Volcano” mechanism.

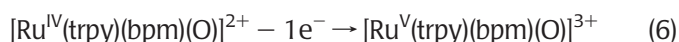
A potential I2M bimolecular mechanism is discarded based on the labeling experiments.

3.1.2. The [Ru(trpy)(B)(H₂O)]²⁺ Complexes. Recently, Meyer’s group¹³ reported a couple of mononuclear Ru^{II}–H₂O complexes of the general formula [Ru^{II}(trpy)(B)(H₂O)]²⁺, where B represents the bidentate chelating ligands bpm (2,2'-bipyrimidine) and bpz (2,2'-bipyrazine) and trpy is the tridentate meridional ligand 2,2':6',2''-terpyridine. These complexes are capable of oxidizing water to dioxygen in a highly efficient manner. Whereas in most Ru^{II}–OH₂ complexes the removal of protons

and electrons takes place in a sequential manner, in the case of the complex containing the bpm ligand oxidation state III is not stable and the oxidation takes place directly by a 2e[−] process



This is a phenomenon that has been previously reported for other Ru^{II}–OH₂ complexes and that is strongly dependent on the electronic nature of the ligands bonded to Ru.¹⁴ Further oxidation again to even higher oxidation states is clearly observed electrochemically and occurs at a reasonable potential as shown in the following equation:



Once the oxidation state V is reached, this species is now highly reactive and suffers a WNA that generates the O–O bond, forming a Ru^{III}–OOH intermediate as shown in Figure 2 (left), where the proposed mechanism for water oxidation is represented. Then the Ru^{III}–OOH intermediate undergoes a rapid 1e[−] oxidation accompanied by proton loss to form a Ru^{IV}–OO that finally generates dioxygen; the latter is the rate determining state. This mechanism has been elucidated by means of a detailed kinetic analysis monitored by UV–vis spectroscopy. As in the previous case, it is also interesting here to plot the formal oxidation state of Ru metal for the different intermediate species that participate in the catalytic cycle as function of the reaction evolution. This is depicted in Figure 2 (right), and as it can be observed the graph resembles a rollercoaster and thus is termed the “Rollercoaster” mechanism.

3.1.3. The Ru^{II}N₆ Type of Complexes. Also, very recently, Thummel’s group¹⁵ reported a series of Ru mononuclear complexes that upon addition of an excess of Ce(IV) are capable of oxidizing water to dioxygen in a catalytic manner. Of this series of complexes, two of them are especially interesting, the [Ru^{II}(trpy)(4-pic)₃]²⁺ and the [Ru^{II}(trpy)(bpy)(4-pic)]²⁺ (4-pic = 4-methylpyridine), given the absence of an aqua group and the saturated first coordination sphere of a d⁶ Ru^{II}N₆ type of complex. Even though there is no detailed experimental mechanistic information available, it is proposed that the water oxidation mechanism proceeds via a metal coordination expansion to seven with one incoming solvent water as shown in Figure 3. The critical O–O bond formation step is proposed to involve an additional solvent water to the generated higher oxidation state [Ru^V(trpy)(4-pic)₃(O)]⁴⁺, that generates a Ru–OOH intermediate that finally evolves dioxygen and the initial Ru^{II} species in a “Volcano” mechanism. The mechanistic proposal is supported by density func-

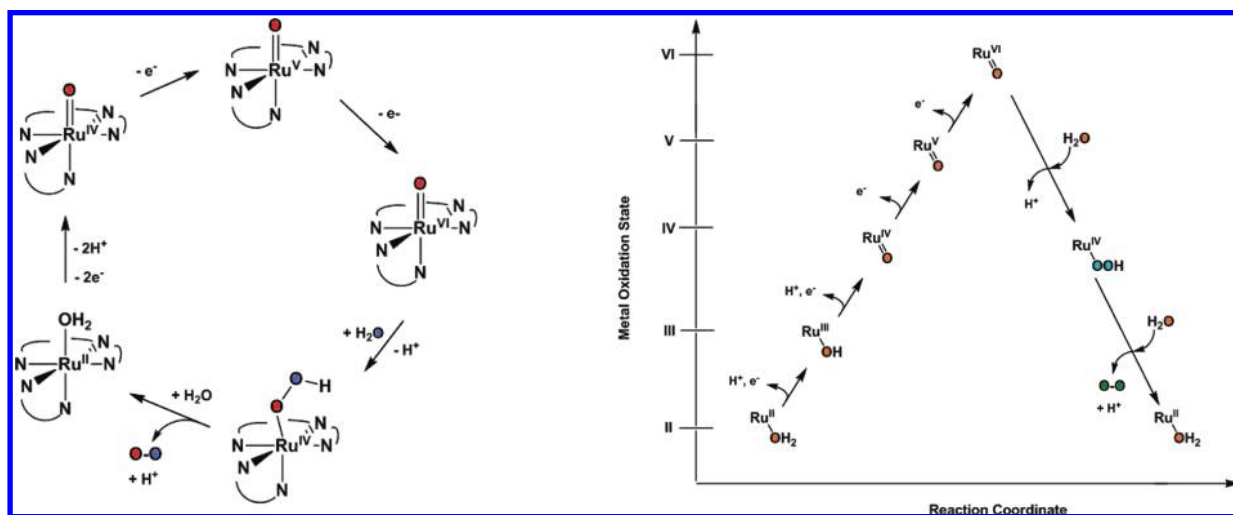


FIGURE 1. (left) Proposed reaction mechanism for $[\text{Ru}^{\text{II}}(\text{DAMP})(\text{bpy})(\text{H}_2\text{O})]^{2+}$. The DAMP is represented as N–N–N, whereas the bpy is represented by N–N. Colors of O-atoms symbolize ^{16}O or ^{18}O labeling. (right) Plot of the formal Ru oxidation state versus the species generated along the reaction coordinate. “Volcano” mechanism. O-atom colors follow the same label as those in Table 1 and will be used for all the other figures.

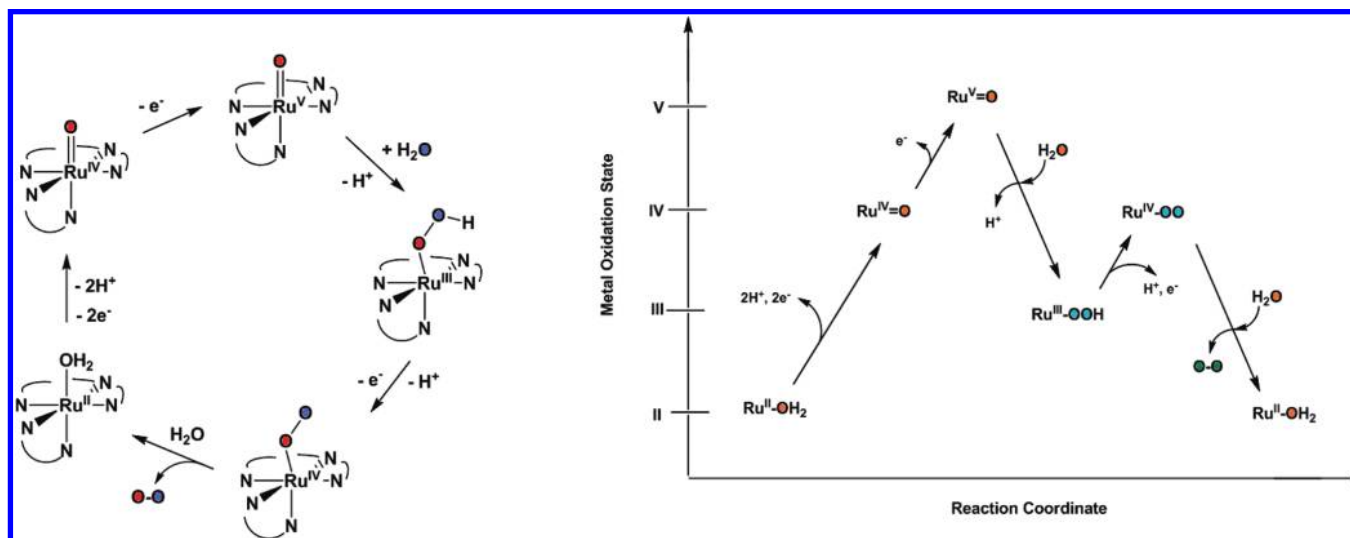


FIGURE 2. (left) Proposed reaction mechanism for $[\text{Ru}^{\text{II}}(\text{trpy})(\text{bpm})(\text{H}_2\text{O})]^{2+}$. The trpy is represented as N–N–N, whereas bpm is represented by N–N. (right) Plot of Ru formal oxidation state versus the species generated along the reaction coordinate. “Rollercoaster” mechanism.

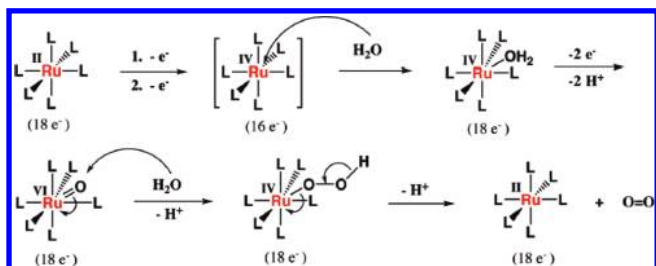


FIGURE 3. Seven-coordinated water oxidation mechanism proposed for $[\text{Ru}^{\text{II}}(\text{trpy})(4\text{-pic})_3]^{2+}$ and $[\text{Ru}^{\text{II}}(\text{trpy})(\text{bpy})(4\text{-pic})]^{2+}$. Reprinted with permission from ref 15. Copyright 2008 American Chemical Society.

tional theory (DFT) calculations that yield reasonable energies for the proposed intermediate species.

The seven-coordination proposal is further supported by the fact that after the catalytic reaction the first coordination

sphere of the complex remains intact and by the need to have reactive Ru–OH₂ groups that lower potentials and that upon reaching higher oxidation states can form O–O bonds. It is important to bear in mind here that the RuN₆ type of complexes such as Ru(trpy)₂²⁺ or Ru(bpy)₃²⁺ have redox potentials in the range of 1.1–1.3 V vs SCE for their Ru^{III}/Ru^{II} couple, and that in the following oxidation state the Ru^{IV}/Ru^{III} couple is beyond the solvent oxidation limits.

3.2. Polynuclear Complexes. Polynuclear complexes are in general more difficult to prepare and characterize than the corresponding mononuclear complexes, and the nature and properties of the complex will be strongly dependent on the BL. The BL will be responsible for the degree of electronic coupling between the metal centers¹⁶ and thus can strongly influence the

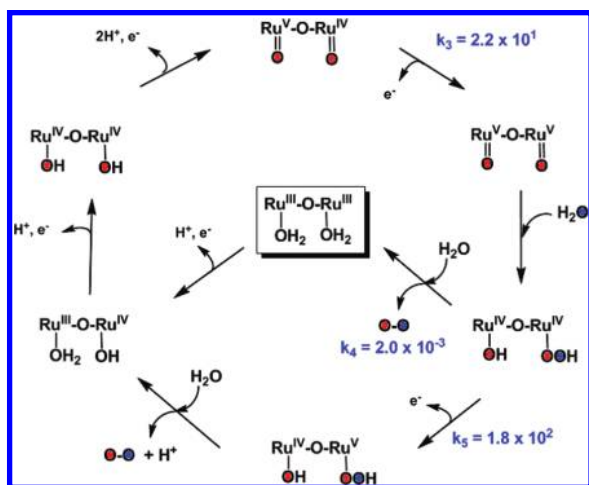
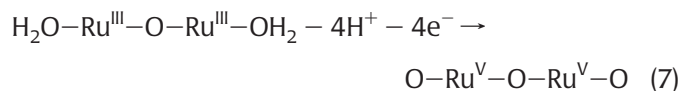


FIGURE 4. Metal based reaction mechanisms proposed for the blue dimer. Rate constants are expressed in $\text{M}^{-1} \cdot \text{s}^{-1}$ for k_3 and k_5 and in s^{-1} for k_4 . Bpy ligands are not drawn.

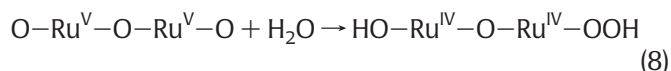
electronic structure of the metal. Furthermore, the BL can also have a certain control of the potential through space interactions of the putative active groups. From a mechanistic perspective, the presence of two or more metal centers in the complex adds further complexity, since even for symmetrical complexes the roles of metals in the catalytic cycle might be different.

3.2.1. The Blue Dimer. In 1985, Meyer's group¹⁷ reported the synthesis, structure, and electrochemical properties of a dinuclear complex *cis,cis*-[(bpy)₂(H₂O)Ru(μ -O)Ru(H₂O)-(bpy)₂]⁴⁺ known as the "blue dimer" because of its characteristic deep blue color ($\lambda_{\text{max}} = 637 \text{ nm}$; $\epsilon = 21\,100 \text{ M}^{-1} \cdot \text{cm}^{-1}$ at pH 1.0). This dimer contains two Ru^{III}-OH₂ groups that are bridged by a dianionic oxido ligand that is responsible for the electronic coupling between the metal centers, manifested by its unique magnetic, spectroscopic, and electrochemical properties.¹⁸ This, in turn, is responsible for its redox properties and by extension for its catalytic behavior. From a structural point of view, it is also important to highlight that the X-ray of this complex gives a torsion angle for the O-Ru-O-Ru-O atoms of 65.7° and that the O-atoms of the aqua groups are situated at 4.72 Å. The blue dimer constitutes a landmark in water splitting because it was the first molecularly well characterized complex that was shown to be capable of oxidizing water to dioxygen. Over the last 20 years, there have been a few mechanistic studies that have been carried in order to understand how the reaction proceeds. In the present Account, we describe a simplified version that contains the latest contributions reflecting the present state of knowledge for this system.¹⁹ Figure 4 shows the mechanism proposed for this reaction using both a stoichiometric amount and an excess of the Ce(IV) oxidant. In both cases, it is proposed a series of 1e⁻ oxidations that in some cases are also

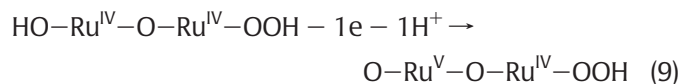
accompanied with proton transfer where the initial Ru^{III}-O-Ru^{III} complex is oxidized to its Ru^V-O-Ru^V oxidation state as summarized in the following equation where the bpy ligands have been omitted



The individual rate constants have also been calculated (Figure 4) and show the last ET process as the slowest process under the excess oxidant pathway. Once this species has been generated, it suffers a nucleophilic attack from solvent water to generate a potential OH-Ru^{IV}-O-Ru^{IV}-OOH intermediate



In the absence of more oxidant, this intermediate releases dioxygen slowly and generates the initial blue dimer in its oxidation state III,III in a "Volcano" mechanism. In the presence of an excess of oxidant, it is proposed that the OH-Ru^{IV}-O-Ru^{IV}-OOH intermediate is further oxidized to the V,IV oxidation state



Now, this V,IV species rapidly releases dioxygen with generation of the IV,III species; in this case, it represents a "Roller-coaster" mechanism.

As mentioned before, in polynuclear complexes, the BL role is critical since is responsible among other issues to establish the degree of communication between metal centers. The blue dimer is a good example of the importance of this influence that can be clearly observed in eq 8, where the oxidation V,V species reacts with oxidized water by 2e⁻ to form a hydroperoxidic intermediate with oxidation state IV,IV, where the two electron oxidation is shared by the two metals. This description of the mechanism raises another important issue that the role of the two metal centers is clearly different, even if the complex possesses C₂ symmetry. While one of the metals is responsible for the O-O bond formation through WNA, the other one mainly acts as an electron shuttle. This cooperative effect allows sharing the burden of multiple ET between the two metal centers and occurs thanks to the electronic coupling of the oxido-BL.

For the blue dimer, Hurst's group proposes that, besides the SWNA mechanism described above, there is a part of the oxidation process that involves the bpy ligands. This is described in section 5.

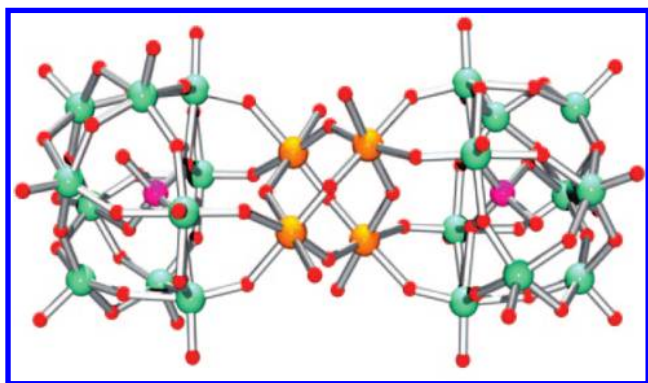


FIGURE 5. POV-Ray drawing of the X-ray structure of $[\text{Ru}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ ($\text{Ru}_4\text{-POM}$).

3.2.2. The $\text{Ru}_4\text{-POM}$ Complex. In 2008, the groups of Bonchio and Hill²⁰ reported the water oxidation activity of the complex $\text{Cs}_{10}[\text{Ru}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4(\gamma\text{-SiW}_{10}\text{O}_{36})_2]$ ($\text{Ru}_4\text{-POM}$; POM is the polyoxometalate ligand $\gamma\text{-SiW}_{10}\text{O}_{36}$) whose structure is shown in Figure 5 and that consists of a tetranuclear complex containing four $\text{Ru}^{\text{IV}}\text{-OH}_2$ groups with the POM and bridging OH^- and O^{2-} ligands in the first coordination sphere of the metal centers. For this complex, it has been shown that the initial $[\text{Ru}^{\text{IV}}\text{-OH}_2]_4$ core is oxidized by four successive steps to form the $[\text{Ru}^{\text{V}}\text{-OH}]_4$ species. The latter reactive species, based on kinetics and DFT calculations, is proposed to undergo a WNA to form a hydroperoxidic intermediate that later evolves dioxygen in a “Volcano” mechanism. The mechanistic proposal relies on the fact that the oxygen evolution process is first order with regard to the catalysts and the unlikelihood that a deca-anionic species could undergo a bimolecular process. This complex constitutes another example of a cooperative effect, in this case shared by four metal centers, and manifests the enormous possibilities to design water oxidation catalysts containing a wide range of bridging and ancillary ligands.

4. Interaction of Two M–O Units (I2M)

The interaction of two $\text{Ru}\text{-O}$ units can potentially take place both in an intramolecular manner with complexes containing two $\text{Ru}\text{-O}$ units and in a bimolecular process with complexes containing only one $\text{Ru}\text{-O}$ unit. The former is described herein, whereas for the latter no examples have been reported in the literature yet.

4.1. The *in,in*- $\text{Ru}\text{-Hbpp}$ Complex. The *in,in*- $\{[\text{Ru}^{\text{II}}(\text{trpy})(\text{H}_2\text{O})_2(\mu\text{-bpp})]^{3+}(\text{in,in}\text{-Ru}\text{-Hbpp})\}$ complex consists of a dinucleating 3,5-bis-(2-pyridyl)pyrazolate anionic ligand (bpp^-) that acts as a backbone (see Scheme 1) for the Ru metal centers, placing them in close proximity and further providing a route for electronic coupling between them. In addition, the ancil-

lary trpy ligands occupy three meridional positions in such a way that the sixth coordination is occupied by oxygen atoms of aqua groups.²¹ This arrangement places the two O-atoms at 2.48 Å (sum of the van der Waals radii is 3.04 Å), producing a through space supramolecular interaction. Indeed, NMR analysis for this complex exhibits C_{2v} symmetry, suggesting that there is a fast exchange process that interconverts the enantiomeric forms associated with aqua positions above and below the plane of the pyrazolate moiety. Addition of excess Ce(IV) to this complex generates dioxygen efficiently, and the mechanism was investigated by means of kinetic analysis followed by UV–vis spectroscopy and ^{18}O labeling experiments.²²

The II,II species is sequentially oxidized by a $1e^-$ process with Ce(IV) up to the IV,IV oxidation state. At this stage, the complex advances to an intermediate that later on evolves dioxygen. Initially, two “Volcano” mechanisms with cooperative effects were considered, namely, (a) WNA (Figure 6, left) with the formation of a hydroperoxidic intermediate that later progresses toward the generation of dioxygen and the formation of the initial catalyst and (b) an I2M process (Figure 6, right) that forms a $\mu\text{-}1,2\text{-peroxo}$ intermediate that is followed by the formation of also a hydroperoxidic intermediate that finally generates oxygen. Oxygen labeling experiments with H_2^{18}O unambiguously show that the only mechanism occurring in this system is the intramolecular process. The mechanistic proposal is further supported by a thorough theoretical analysis of intermediates and transition states based on DFT and CASPT2 calculations.²³ A bimolecular process was discarded based on the first order kinetics found for the formation of the intermediate and based on the ^{18}O labeling results.

4.2. The Ru-Pincer Complex. Recently, the Milstein group reported a mononuclear Ru complex containing an unsymmetric tridentate meridional ligand 2-(di-*tert*-butylphosphino-methyl)-6-diethylaminomethyl)pyridine (PNN, see Scheme 1), two OH^- groups in a *cis* fashion, and a carbonyl complex completing the octahedral type of coordination; see Figure 7.²⁴ Irradiation of this complex with 320–420 nm range produces HOOH that later on catalytically disproportionates to dioxygen and water. Even though in this system HOOH is released, and thus the thermodynamic demands are higher than those for the $4e^-$ oxidation to generate O_2 , mechanistically the process is very interesting. Oxygen labeling experiments with ^{18}O together with kinetic analysis clearly indicate that the formation of the O–O bond proceeds in an intramolecular fashion involving a reductive elimination process where Ru changes oxidation state from II to 0.

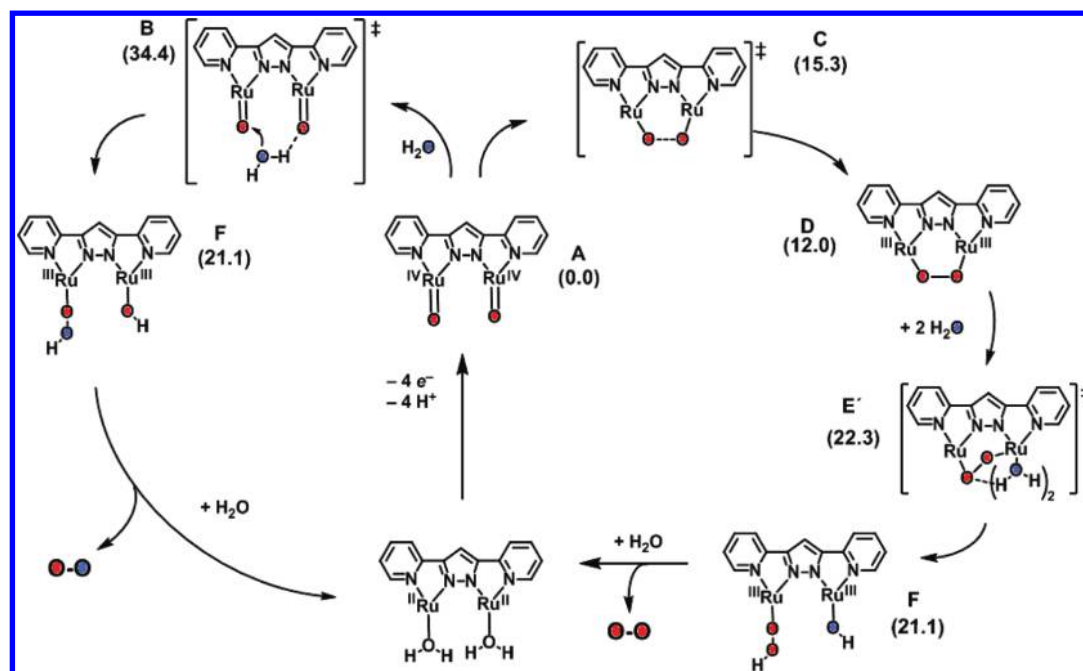


FIGURE 6. Potential water oxidation pathways for the *in,in*-Ru-Hbbp complex: (left) WNA and (right) I2M. Trpy ligands are not shown.

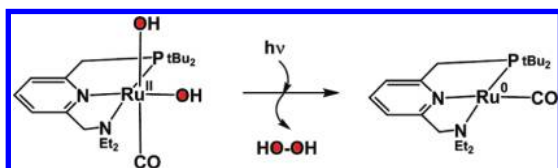
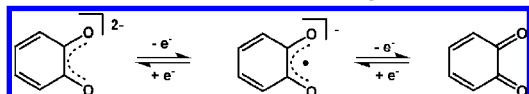


FIGURE 7. Drawing of the structure of $[\text{Ru}^{\text{II}}(\text{OH})_2(\text{PNN})(\text{CO})]$ and its evolution under light irradiation.

SCHEME 3. Redox States of the Quinone Ligand



5. Redox Noninnocent Organic Ligands

Catechols are known for being relatively easily oxidized by a sequential $1e^-$ loss to form the corresponding semiquinones and quinones as shown in Scheme 3. The combination of $\text{Ru}-\text{OH}_2$ groups and redox active ligands make the system complex but particularly interesting for multiple ET redox transformation such as the oxidation of water to molecular dioxygen. This strategy was reported by Tanaka et al. some years ago²⁵ while preparing the complex $\{[\text{Ru}^{\text{II}}(\text{OH})(\text{Q})]_2(\mu\text{-btpyan})\}^{2+}$, where btpyan is a dinucleating trpy based ligand bridged by an anthracene group (1,8-bis(2,2':6',2''-terpyridyl)-anthracene; see Scheme 1) and the rest of the coordination positions are occupied by a 3,6-di-*tert*-butyl-1,2-benzoquinone (Q), a redox active ligand, and by a hydroxo group. It was shown that upon applying a sufficiently high redox potential the complex is capable of oxidizing water to dioxygen with a high turnover number. Recently, a DFT calculation made in

collaboration with the groups of Fujita and Muckerman²⁶ has been performed and is depicted in Figure 8 (left). It is interesting to see the redox inactivity of the Ru centers; in other words, all the ET processes that are proposed to lead to the formation of O_2 from water are based on the quinone ligand. It is also interesting to highlight here that the O–O bond formation takes place via an I2M mechanism between a $\text{Ru}^{\text{II}}-\text{O}\cdot$ (oxyl) and a $\text{Ru}^{\text{II}}-\text{OH}$ to form a superoxide concomitant with a $1e^-$ reduction of each Q to Q^{-1} .

For the blue dimer, there were several mechanistic studies carried out by Hurst and Cape²⁷ that propose the involvement of bpy ligands in the formation of the O–O bond as is depicted in Figure 8 (right). This mechanism is proposed to occur when the dimer in its $\text{Ru}^{\text{V}}=\text{O}$ form reacts with a solvent water that adds to one of the pyridyl rings of a bpy forming a coordinated bpy radical that further adds one more water forming a *cis*-dihydroxyl-bpy that is responsible for the formation of the O–O bond that finally produces dioxygen and the initial Ru complex closing the catalytic cycle.

6. Conclusions and Future Perspectives

In the absence of redox active ligands, it is interesting to realize here that all the water oxidation catalysts described so far that undergo a WNA mechanism have high oxidation states $\text{Ru}(\text{V})$ and $\text{Ru}(\text{VI})$. This suggests that such high oxidation states for Ru need to be stabilized by the oxygen atom of the $\text{Ru}-\text{O}$ group, rendering it highly electrophilic and thus favoring the nucleophilic attack of a solvent water molecule. On the other hand, a

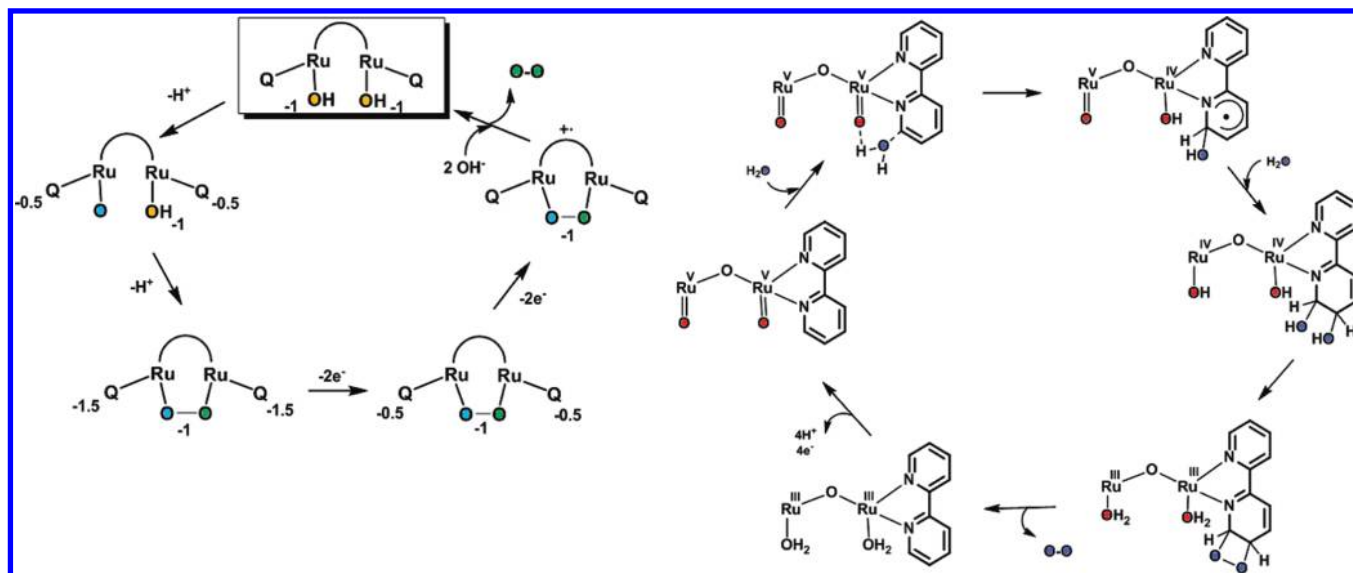


FIGURE 8. Proposed ligand based mechanisms (left) for the $\{[Ru^{II}(OH)(Q)]_2(\mu\text{-btpyan})\}^{2+}$ complex (btpyan-BL is represented by an arc) and (right) for the blue dimer.

catalyst that generates dioxygen at Ru(IV) or lower oxidation states, such as Ru-Hbpp, will undergo an I2M mechanism. Therefore, for a Ru–H₂O catalyst, the electronic nature of the auxiliary ligands that completes its first coordination sphere is crucial. Strong electron donating ligands such as the dianionic oxido ligand will allow access to higher oxidation states and thus will favor the WNA mechanism. This is the case of the blue dimer and also of the Ru-POM complex. Furthermore, this also suggests that modification of ligands with electron donating or electron withdrawing groups, without modifying the intrinsic coordination properties of the original ligand, might be capable of altering the nature of the reaction mechanism.

Another important issue here is that when a water oxidation catalyst contains more than one Ru–OH₂ group, the role of the metal centers can be radically different. This is exemplified for the case of the Ru-POM where one of the Ru–OH₂ will be responsible for the O–O bond formation steps whereas the role of the other centers will merely be as electron shuttles. Therefore, the design of a tailored nonsymmetric catalyst where the different needs of the metal could be controlled will certainly enhance the performance of the complex. A key role for polynuclear complexes is obviously played by the BL that will decide the degree of electronic communication between metal centers and thus will be responsible for paving the way to rapid ET. Furthermore, the BL also allows controlling the potential through space interactions among the Ru–O groups. An example of this is the *in,in*-Ru-Hbpp complex where the O atoms are situated only 2.48 Å apart and thus favor the intramolecular process. However, in the corresponding *out,out*-Ru-Hbpp isomer, the intramolecular process

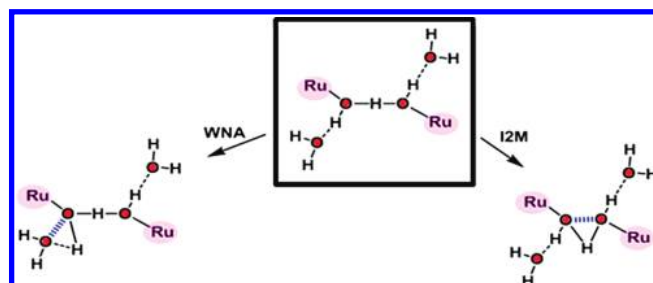


FIGURE 9. Potential mechanism proposed for the evolution of $\{[Ru^{IV}(bdc)(4\text{-pic})_2](\mu\text{-}(HOHOH))\}[PF_6]_3 \cdot 2H_2O$ (the bdc and 4-pic ligands are not shown).

will not take place and the O–O bond formation step is expected to proceed via a bimolecular mechanism.

Finally, Sun's group²⁸ has prepared an octahedrally distorted Ru complex containing a tetradentate N₂O₂ dianionic ligand (bdc²⁻ is the 2,2'-bipyridine-6,6'-dicarboxylate ligand) that constrains the equatorial coordination around the metal center while the two axial position are occupied by 4-picoline ligands. Treatment of this complex with excess Ce(IV) generates dioxygen in a catalytic manner. During the course of water oxidation, a seven-coordinate Ru^{IV}–OH₂ dimer intermediate was obtained and characterized, $\{[Ru^{IV}(bdc)(4\text{-pic})_2](\mu\text{-}(HOHOH))\}[PF_6]_3 \cdot 2H_2O$. The hydroxo groups are situated in the equatorial plane and are part of the HOHOH⁻ BL, while the water molecules are interacting with the HOHOH BL group via hydrogen bonding as can be observed in Figure 9. This complex is interesting since, even though a detailed mechanistic work has not been carried out, it seems to be situated at the crossroads of the WNA and the I2M mechanisms. As indicated in Figure 9, slight modifications of key O–H bonds will drive the intermediate to one or the other pathway.

In spite of the intrinsic experimental difficulties associated with the elucidation of reaction mechanisms for catalytic water oxidation, the basic elements needed to describe its landscape are just unfolding. The topography of this landscape delineates a few O–O bond formation routes running through hills and valleys that are extremely useful for designing future water oxidation catalysts. Furthermore, a few pitfalls are also pointed out that need to be observed to come up with an ideal water oxidation catalyst.

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FOOTNOTES

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