Role of ligands in catalytic water oxidation by mononuclear ruthenium complexes

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ABSTRACT: Since first reported in 2005, mononuclear ruthenium water oxidation catalysts have attracted a great deal of attention due to their catalytic performance and synthetic flexibility. In particular, ligands coordinated to a Ru metal center play an important role in the catalytic mechanisms, exhibiting significant impact on catalyst efficiency, stability and activity towards water oxidation. This review focuses on finding possible correlation between the ligand effects and activity of mononuclear Ru aqua and non-aqua complexes as water oxidation catalysts. The ligand effects highlighted in the text include the electronic nature of core ligands and their substituents, the trans-cis effect, steric hindrance and the strain effect, the net charge effect, the geometric arrangement of the aqua ligand and the supramolecular effects, e.g., hydrogen bonding and influence of a pendant base. The outcome is not always obvious at the present knowledge level. Deeper understanding of the ligand effects, based on new input data, is mandatory for further progress towards a rational development of novel catalysts featuring enhanced activity in water oxidation.

1. **Introduction**

Natural photosynthesis, conducted mainly by green plants, can efficiently convert solar photoenergy into chemical energy in a clean and sustainable way. In this process, water as a starting material is catalytically oxidised to O2 (Equation 1) by the oxygen-evolving complex (OEC) of MnCaO5 in Photosystem II [[[1]](#endnote-1),[[2]](#endnote-2),[[3]](#endnote-3)]. Therefore, manganese-based oligonuclear complexes were initially applied to mimic natural systems [[[4]](#endnote-4),[[5]](#endnote-5)].

(1)

The family of multinuclear ruthenium complexes became very attractive since the first water oxidation catalytic activity of the ‘blue dimer' reported by Meyer and co-workers [[[6]](#endnote-6),[[7]](#endnote-7)]. However, at least two metal center containing frameworks were believed to be necessary for catalytic water oxidation until the first series of mononuclear ruthenium water oxidation catalysts were demonstrated by Thummel and co-workers in 2005 [[[8]](#endnote-8)]. These results have suggested that the single metal center is catalytically active enough for water oxidation and this observation opened the door for the development of a new series of systems with catalytic activity and synthetic flexibility. Thus, the range of water oxidation catalysts based on transition metal complexes has been significantly enlarged, not only including oligonuclear Mn and Ru series, but also the related mononuclear species and complexes of iridium, iron and cobalt [[[9]](#endnote-9),[[10]](#endnote-10),[[11]](#endnote-11),[[12]](#endnote-12),[[13]](#endnote-13),[[14]](#endnote-14),[[15]](#endnote-15),[[16]](#endnote-16),[[17]](#endnote-17),[[18]](#endnote-18)]. In particular, the corresponding catalytic mechanisms, kinetics, and activity towards water oxidation have been reviewed. However, the effects of the ligand design and variation on the catalytic efficiency, catalyst stability and activity have not been comprehensively discussed and reviewed so far.

This review is thus mainly focused on evaluating the ligand impact on the activity of different recently reported Ru mononuclear water oxidation catalysts (WOCs) by comparison of the initial turnover frequencies (TOFs) and turnover numbers (TONs). Both TOF (see Berlinguette et al. [[[19]](#endnote-19)]) and TON (see Thummel at al. [8]) values have been used to rank catalytic activity for WOCs triggered electrochemically and chemically (in the latter case with cerium(IV) as the strong sacrificial oxidant). In order to better correlate the catalytic performance, the activity of a catalyst is evaluated, where possible, in terms of its TOF to avoid limitations of TON arising from catalyst degradation pathways.

**2. Mononuclear Ru aqua complexes for water oxidation**

An aqua ligand directly bound to the metal center in mononuclear Ru(II) WOCs plays a key role in proton coupled electron transfer (PCET) during oxidation. The increased acidity of the coordinated aqua ligand in the Ru(III) oxidation state induces deprotonation, reducing the oxidation potentials by avoiding positive charge build-up and producing the two-electron oxidized Ru(IV) species stabilized by the formation of the Ru=O bond [[[20]](#endnote-20),[[21]](#endnote-21),[[22]](#endnote-22)]. These Ru(II) WOCs are capable of reaching the higher oxidation states within a relatively narrow potential range. Several examples of pseudoctahedral mononuclear aqua-Ru WOCs are known in which the aqua ligand is either equatorial or axial.

*2.1. Ruthenium complexes with an equatorial aqua ligand*

The first three examples of mononuclear ruthenium water oxidation catalysts were reported by Thummel and co-workers in 2005 [8]. The complexes (Chart 1, **1a-c**) contain two axial 4-substituted pyridines and two equatorial ligands. In the equatorial plane, the metal center directly binds to a tridentate ligand and the fourth coordination site is occupied by a water molecule through a Ru―O bond. Single-crystal X-ray analysis has revealed that the water molecule is further stabilized through H-bonding to an uncomplexed naphthyridine nitrogen. All three complexes show catalytic activity toward water oxidation. The axial pyridine ligand with the NMe2 substituent in the para position is the strongest σ-donor in the series, showing the highest catalytic activity (**1a**: TOF = 7.8×10-4 s-1, **1b**: TOF = 3.5×10-4 s-1 and **1c** = = 3.5×10-4 s-1); however, the complex **1b** with the 4-picoline axial ligands presents the highest stability (**1a**: TON = 50, **1b**: TON = 580 and **1c**: TON = 70). This observation reflects the effect of the strongly acidic reaction conditions (pH 1) under which the dimethylamino group in complex **1a** becomes protonated, thus acting as electron acceptor instead of electron donor.



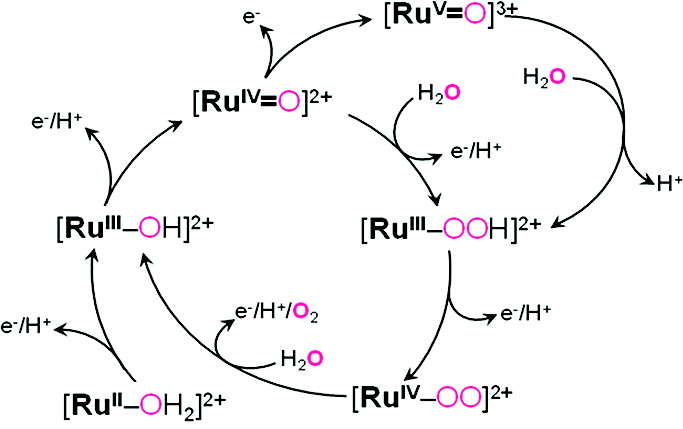
**Chart 1**

Thummel [[[23]](#endnote-23),[[24]](#endnote-24),[[25]](#endnote-25)] and Fujita [[[26]](#endnote-26)] also presented other examples of mononuclear Ru WOCs containing an equatorial aqua ligand having the same general formula [Ru(NNN)(N)2(H2O)] where NNN and N stand for tridentate and monodentate *N*-bound ligands, respectively (Chart 2, complexes **2-4**). For example, complex **2** bears a benzo-1,8-dinaphthyridyl ligand in the equatorial plane and the complexed water molecule is thus able to form a H-bond with the non-coordinated naphthyridine nitrogen. The two *tert*-butyl groups in the 7′ positions at the 1,8-naphthyridine ring in complex **3** prevent possible dimerization. By contrast, the equatorial tridentate ligand encountered in **4** is ordinary 2,2′,6′,2″-terpyridine featuring no sites capable of forming a H-bond with the coordinated water ligand. Complexes **2**, **3** and **4** showed similar catalytic water oxidation activities compared to that of complex **1**. With this idea in mind, complex **5** was designed to bind the potentially equatorial tetradentate ligand as tridentate, one of the uncoordinated pendant aza-aromatic terminals being available to form a hydrogen bond with the equatorial aqua ligand (Chart 2). However, the ligand undergoes a significant distortion, binding actually as tetradentate to the Ru center. Therefore, the true structure of complex **5** only exhibits pyridyl-type ligands and no equatorial aqua ligand. Similar observations were also made for the *N*-methylimidazole and *N*-methylbenzimidazole derivatives that were initially supposed to undergo even stronger distortion and serve as tridentate ligands. These complexes are also available for water oxidation catalysis and details will be discussed in the following section.



**Chart 2**

Detailed mechanistic studies of water oxidation catalyzed by complexes **1** and **2** were initially reported by Fujita et al. in 2011 [[[27]](#endnote-27)] and 2013 [26]. They suggested a pH-dependent catalytic mechanism based on [RuIV=O]2+, which included a ‘non-direct’ water nucleophilic attack (WNA) pathway via [RuV=O]3+ and a ‘direct’ PCET pathway, both resulting in [RuIII―OOH]2+ (Scheme 1). The next step creates an O―O bond in the intermediate [RuIV―OO]2+ that concomitantly releases dioxygen. Supported by electrochemistry, UV-Vis and resonance Raman spectroscopy, pulse radiolysis, stopped flow kinetics, ESI-MS, H218O labelling experiments and theoretical calculations, [RuIV=O]2+ was identified as the key intermediate for complex **1** involved in two PCET processes over a wide pH range. The [RuV=O]3+/[RuIV=O]2+ couple was observed at 1.42 V vs. NHE independently of pH. At pH < 1, the catalytic wave was shifted to a lower electrode potential, overlapping with [RuIV=O]2+ oxidation. By contrast, the electrochemical production of [RuIII―OOH]2+ directly from [RuIV=O]2+ was dominant in neutral and alkaline media. It occurred at 0.7 V vs. NHE, i.e., 0.45 V more negatively than the RuIV=O/RuII―OH2 couple; the ‘direct’ pathway is thus followed.



**Scheme 1.** Proposed mechanism of catalytic water oxidation by complexes **1** and **2**. Reprinted with permission from ref. [27]. Copyright (2011) American Chemical Society.

Neutral mononuclear Ru WOCs **6** and **7** (Chart 3) were prepared and reported by Åkermark and co-workers [[[28]](#endnote-28)]. These Ru(III) complexes coordinate an anionic tridentate ligand through imidazole and phenolate moieties that may trigger PCET reactions and result in formation of species in higher oxidation states at low potentials. In particular, the imidazole site is expected to act as both redox and proton transfer mediator, contributing to the observed catalytic water oxidation. Complex **6** showed high TOF (> 7 s-1) and TON (4000) with [Ru(bpy)3]3+ used as the sacrificial oxidant. However, replacing catalyst **6** with **7** led to significant decrease in the TOF and TON values, probably due to sensitivity of the latter catalyst to oxygen generated along the catalytic path.

The remaining binding site in the equatorial plane of complexes **6** and **7** is occupied by 4-picoline or a water molecule. However, these WOCs favor a 4-picoline-water ligand exchange in aqueous medium where the equatorial picoline ligand can be gradually replaced by water. The catalytic water oxidation by complexes **6** and **7** was explored by electrochemistry and high-resolution mass spectrometry. In particular, the active high-valent intermediate [RuV=O] was observed during the catalytic cycle, suggesting a WNA mechanism. The formation of both oxidized species, Ru(IV) and Ru(V), was influenced by the variation of pH, indicating that PCET processes were involved (Scheme 2). This type of RuV=O intermediate is also assumed to participate in the mechanism of water oxidation by the catalyst **4** [25].



**Chart 3**

**Scheme 2.** Likely mechanism of catalytic water oxidation triggered by oxidized complexes **6** and **7**. Reproduced with permission from ref. [28]. Copyright (2012) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

*2.2. Ruthenium complexes with an axial aqua ligand*

Mononuclear Ru WOCs containing an axial aqua ligand are usually in the form of [Ru(NNN)(NN)(H2O)] where NNN and NN are tri- and bidentate ligands, respectively. The initial investigation into this family of Ru WOCs was carried out by Meyer’s group on complexes **8a** and **8b** in 2008 [[[29]](#endnote-29)] and Sakai et al*.* on complex **8c** in 2009 [[[30]](#endnote-30)] (Chart 4). Moreover, the detailed water oxidation mechanistic scheme was completely defined through further studies on PCET and high-valent intermediates of this series of mononuclear Ru WOCs by Meyer and co-workers [29,[[31]](#endnote-31),[[32]](#endnote-32),[[33]](#endnote-33),[[34]](#endnote-34),[[35]](#endnote-35)].

As illustrated in Scheme 3, three possible pathways have been distinguished for catalytic water oxidation by **8b**, [Ru(tpy)(bpz)(H2O)]2+ (tpy = 2,2′:6′,2″-terpyridine and bpz = 2,2′-bipyrazine) [35]. Under acidic and weakly basic conditions, an initial 2e-/2H+ PCET process converts [RuII(tpy)(bpz)(H2O)]2+ ([RuII―OH2]2+) to [RuIV(tpy)(bpz)(O)]2+ ([RuIV=O]2+), which is followed by an electron transfer step producing [RuV(tpy)(bpz)(O)]3+ ([RuV=O]3+), either electrochemically or chemically with Ce(IV) added as the oxidant. The oxidation state Ru(III) is bypassed because of its thermodynamic instability, arising from stabilization of Ru(II) provided by dπ(RuII)―π\*(bpz) backbonding that increases *E°′* for the Ru(III/II) couple above *E°′* for the Ru(IV/III) couple [[[36]](#endnote-36),[[37]](#endnote-37)]. A peroxido form of [RuIII(tpy)(bpz)(OOH)]2+ ([RuIII―OOH]2+) can be generated from the reaction between the intermediate of [RuV=O]3+ and H2O. After the O―O coupling, [RuIII―OOH]2+ can further be converted into [RuIV(tpy)(bpz)(O2)]2+ ([RuIV―OO]2+) by one-electron oxidation, giving a seven-coordinate structure with a η*2*-bound peroxido ligand. Concomitant decomposition of [RuIV―OO]2+ leads to a release of O2 and recovery of the starting form [RuII―OH2]2+ (pathway 1). Interestingly, the catalytic rate of electrochemical water oxidation by such WOCs could be enhanced significantly under more basic conditions, upon addition of buffers. This observation supported by quantum mechanical/molecular mechanical (QM/MM) simulations suggested that the added base acts as a proton acceptor, decreasing the energy barrier for the O―O bond formation and, hence, triggering more easily bond formation by a concerted atom-proton transfer (APT).



**Chart 4**

By contrast, an electron transfer from [RuIV―OO]2+ to [RuV(tpy)(bpz)(O2)]3+ ([RuV―OO]3+) turns out to be more competitive under more acidic conditions. Resulting [RuV―OO]3+ can rapidly release O2, bind water and convert to [RuIII(tpy)(bpz)(OH)]2+ ([RuIII―OH]2+) on proton removal. Therefore, the catalytic cycle of pathway 2 is completed when [RuIV=O]2+ is reformed from [RuIII―OH]2+ through another PCET process. At the starting point of the catalytic cycle, the oxidation of [RuII―OH2]2+ to [RuIV=O]2+ is fast and is not the rate limiting step. Two rate limiting steps are expected for this series of catalysts in both pathways. One is first-order in catalyst and zero-order in oxidant, being associated with either rate-limiting [RuV=O](n+1)+ oxo attack on water, *kO-O*, or rate limiting O2 loss from [RuIV―OO]n+, *k4*. The other is first-order in complex and first-order in oxidant. These proposals are in good agreement with either rate-limiting oxidation of [RuIV=O]n+ to [RuV=O](n+1)+, *k2*, or rate-limiting oxidation of [RuIV―OO]n+, *k5* [32]

On the other hand, [RuIII―OH]2+ can be also formed by stoichiometric oxidation of [RuII-OH2]2+ by [RuIII(bpy)3]3+. However, the thermodynamic instability of [RuIII-OH]2+ may lead to its disproportionation to the catalytic intermediate [RuIV=O]2+ and the original species [RuII―OH2]2+ (Equation 2), making pathway 3 also possible.

(2)



**Scheme 3.** Proposed pathways of catalytic water oxidation by complex **8b**, [Ru(tpy)(bpz)(H2O)]2+. Reproduced with permission from ref. [35]. Copyright (2014) American Chemical Society.

The σ-donor/π-acceptor properties of the tri- and bidentate ligands bound in mononuclear Ru WOCs represented by complexes **8**-**10** (Chart 4) play important roles in stabilizing higher metal oxidation states [[[38]](#endnote-38),[[39]](#endnote-39)] and further facilitating water oxidation e.g., by lowering redox potentials, increasing the thermodynamic driving force or decreasing energy barriers [32]. Therefore, smart modification or variation of ligands in WOCs is one of the major challenges in order to further improve the catalytic activity towards water oxidation.

Using the [RuII(tpy)(bpy)(H2O)]2+ scaffold, Berlinguette et al.[19,[[40]](#endnote-40)] and Yagi et al. [[[41]](#endnote-41)] provided direct evidence of how catalytic water oxidation is affected by modified electronic properties of mononuclear aqua-Ru polypyridyl complexes. Electronic modification of the [RuII(tpy)(bpy)(H2O)]2+ scaffold was achieved by decorating the bpy and tpy ligands with various electron-withdrawing and donating substituents (Chart 5, complexes **11**-**22**). From these studies, the aqua species [RuII―OH2]2+ was confirmed as the active catalyst in the dioxygen evolution process; an induction period is required by the [RuII―Cl]+ pre-catalyst species to convert into the aqua form. In particular, the rate of the chloride-water ligand exchange depends upon the electron-donating ability of substituents on the polypyridyl ligands. However, the catalytic activity of [RuII―OH2]2+ is sensitive to the solvent medium and is significantly inhibited when competing solvents or anions (e.g., acetonitrile or chloride) are present.



**Chart 5**

Further, the intrinsic relationships between catalytic reactivity and stability and the nature of the electronic properties of the substituent groups on both tpy and bpy ligands were explored. In the initial PCET step, the presence of strongly electron-withdrawing groups on the bpy ligand resulted in higher reaction rates, as they stabilized the low oxidation states of the catalysts. In the following O2 evolution step, electron-withdrawing groups, in general, suppressed the catalytic activity (e.g., TOFs decrease in the order **13b** > **8c** > **16b** > **19b**, see Table 1), but increased the catalyst stability (TONs increase in the same order **13b** **<** **8c** < **16b** ≈ **19b**, see Table 1). Interestingly, catalytic stability is eliminated by the presence of electron-withdrawing groups on the tpy ligand instead of the bpy ligand. Presumably, the compromised π-back-bonding to the bpy ligand due to electron-withdrawing groups on the tpy ligand is responsible. By contrast, electron-donating groups on the bpy ligand show converse effects, that is (a) increasing catalytic rate (e.g., TOFs increasing in the order **12b** < **13b** < **14b**, see Table 1), and (b) reducing catalyst stability (TONs decreasing in the same order **12b** > **13b** > **14b**, see Table 1). The TOF trend can be explained by the additional electron density on the Ru center from the electron-donating groups under strongly oxidative conditions, stabilizing high oxidation states in the O―O formation step or the O2 release process. The TON trend is a consequence of dissociation of the bpy ligand after a certain catalytic oxidation period because the Ru―Nbpy bond trans to the O atom is weakened in high oxidation states.

**Table 1.** Summary of the kinetics of O2 evolution for complexes **8a**, **8c**, **12b**, **13b**, **14b,** **16b** and **19b**.

|  |  |  |
| --- | --- | --- |
| **Complex** | **TOF ( × 10-4 s-1)** | **TON** |
| **8a** | 6.0 | 50 |
| **8c** | 5.1 | 320 |
| **12b** | 5.2 | 200 |
| **13b** | 11.0 | 100 |
| **14b** | 12.0 | 60 |
| **16b** | 2.6 | 480 |
| **19b** | 2.0 | 460 |

Data obtained from ref. [19]. TOF is the first-order rate constant (±10%) extracted by an exponential fitting of O2 evolution data as a function of time and TON is catalytic turnovers after 3 h.

Similar substituent effects were also observed within a series of pre-catalysts, [RuII(tpy-R)(phen-X)Cl]+, where tpy-R is the tridentate 4′-(4-methylmercaptophenyl)-2,2′:6′,2″-terpyridine ligand and phen-X is 1,10-phenanthroline, either unsubstituted or bearing 5-nitro, 5,6-dimethyl and 3,4,7,8-tetramethyl substituents [[[42]](#endnote-42)]. Again, enhanced catalytic reactivity (TOF) for water oxidation was observed when an electron-donating rather than electron-withdrawing substituent was attached to the 1,10-phenanthroline ligand. Surprisingly, the reported process of chloride-to-aqua ligand exchange was not observed for these pre-catalysts during the induction period and the chloride-forms of pre-catalysts could be fully recovered after catalysis. This may indicate that the WNA prefers a high oxidation state (obtained on addition of Ce(IV)) rather than being associated with the Ru(II) species. The chloride binding to the more electrophilic Ru center in high oxidation states would make the Ru―Cl bond less easily broken.

On a different note regarding ligand variation, strong π-acceptor 2,2′-bipyrimidine was introduced in complex **8a** [32]. The enhanced electron-withdrawing ability of the chelating ligand resulted in higher oxidation potentials and lower TON values in comparison with **8c**, [Ru(tpy)(bpy)(H2O)]2+. However, the energy difference in the bond forming step with **8a** is actually considerably smaller than that with **8c**. Direct support for this observation can be obtained from the difference in the rate constants for the rate limiting step for **8a** (7.5×10-4 s-1) and **8c** (1.9×10-4 s-1). Based on results of computational studies, population analysis shows less electron density at the reactant Ru―O bond when more nitrogen atoms (Chart 4) are contained in the chelating ligand structures, lowing the energy needed to form the O―O bond [[[43]](#endnote-43)].

Ru‒carbene catalysts **8d** and **8e**, containing a Ru―(C∩N) chelate ring showed a reduced TON in comparison with corresponding Ru―(N∩N) chelate ring containing catalysts in Chart 4: **8d** ≈ **8e** < **9c** ≈ **8a** < **8c** [32], while they surprisingly exhibiting considerable enhancement of water oxidation reactivity, in contrast to that of **9c**, due to increased driving force for the O―O bond forming step [[[44]](#endnote-44)]. As with the WNA mechanism mentioned above (Scheme 3), the electrocatalytic water oxidation by **8d** involves PCET activation to form [RuV=O]3+; then O―O coupling and finally further oxidation to the peroxido species [RuIV―OO]2+, releasing O2. Compared to **9c**, **8d** shows pH-dependent RuII/III and RuIII/V couples at higher potentials. The former is due to the stabilized Ru(II) center by backbonding to the carbene ligand in the carbene complex. The latter for the consecutive 2e-/2H+ conversion of [RuIII―OH2]3+ to [RuV=O]3+ comes from the higher p*Ka* value of [RuIII―OH2]3+, which results in a 0.1 eV change in RuIII/V couple at pH 1. The increased potential of this redox couple has strong relevance to the O―O formation step and leads to an enhanced driving force for water oxidation to the hydroperoxido form [RuIII―OOH]2+. As mentioned previously, the reactivity of some WOCs can further be improved in a weakly alkaline environment, where the catalytic mechanism is following the APT pathway on addition of proton-acceptor bases, e.g., CH3COO- or H2PO4-. However, this feature is absent for the carbene complex **8d** because its oxidized species [RuIII―OH2]3+ coordinates CH3COO- or HPO42-, forming [RuIII―CH3COO-]2+ or [RuIII―H2PO4-]2+. More recently, Llobet and co-workers have also reported a series of mononuclear aqua-Ru complexes containing a different combination of carbene/pyridyl ligands [[[45]](#endnote-45)]. They revealed an interesting linear correlation between the number of carbene ligands in the complexes and Δ*E1*/2 where each carbene unit causes a 100 mV decrease in the Δ*E1*/2 value. The parameter Δ*E1*/2 is defined as the difference between *E1*/2(RuIV/III) and *E1*/2(RuIII/II) involved in the two PCET processes and the exact values of these two pH-dependent redox potentials can be extracted from Pourbaix diagrams [38]. Higher Δ*E1*/2 values indicate stabilized Ru(III) oxidation states while low values point to facile disproportionation of Ru(III) to the Ru(II) and Ru(IV) oxidation states. Therefore, the capacity to transfer two electrons in a single step is considered to contribute to the electrocatalytic driving force. This correlation may be used as one of the explanations for the enhanced driving force of water oxidation by Ru carbene catalyst **8d** (Δ*E1*/2 = 360 mV) compared to **9c** (Δ*E1*/2 = 470 mV).

Complex **23** (Chart 6) features the 2,2′-diimidazole (H2bim) ligand instead of the commonly utilized 2,2′-bipyridine ligand [[[46]](#endnote-46)]. Much like the aqua ligand in complexes **8b** (Scheme 3) and **23**, also the 2,2′-diimidazole ligand serves as the donor of two protons, undergoing proton dissociation at p*Ka* 9 and 11.3. Then, a four-step [4H+, 4e-] PCET reaction can take place at pH-dependent electrode potentials, as illustrated by the Pourbaix diagram [46], generating the [RuIV(bim)=O]2+ species without electrostatic charge build-up. The multi-electron storage ability and enhanced electron-donor power of the 2,2′-diimidazole result in a lower water oxidation potential, viz. ca. 1.2 V vs. SCE compared to 1.35 V observed for analogous Ru WOCs such as [Ru(tpy)(bpy)(H2O)]2+ [30] and [Ru(tpy)(bpz)(H2O)]2+ [29].

Ligand variation can also be carried out on the tridentate NNN ligand. The series of complexes **24** and **25** (Chart 6) was reported by Sakai and co-workers where the common tpy ligand was replaced by polyamine ligands [[[47]](#endnote-47),[[48]](#endnote-48)]. Compared to terpyridine ligands, polyamine ligands such as 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) exhibit stronger σ-donor properties resulting in considerable negative potential shifts of the RuII/RuIII and RuIII/RuIV couples. However, no significant negative perturbation is observed for the O2-evolution potentials, even if stronger electron-donating substituents (R = OMe) are attached in the 4,4′-positions at bpy ligand. These complexes also show much lower catalytic activity than the model terpyridine complex **8c** (Table 2), hence indicating that the driving force for the O2-evolving oxidation corresponds directly with the catalytic activity for water oxidation in this case. Although these complexes display comparable overpotentials for the O2 evolution, superior to the reference terpyridine complex **8c**, they still show an overpotential trend depending upon the electron-donating character of the substituent groups. As shown in Table 2, more electron-donating substituents lower the overpotential, thereby increasing the O2-evolving activity. Bearing the same substituent, complexes **24** and **25** have very similar O2-evolving activity, but the initial catalytic rate of O2 evolution by **25** is much higher than that of **24**. This probably arises from the difference between sp2 N-atom ligation of the pyrazole ring in **25** and the sp3 N-atom ligation of the amine in **24**. The former ligation results in a much shorter Ru―N distance than the latter, resulting in stronger metal center coordination, and also makes the thermodynamics of the O2 release less endothermic [[[49]](#endnote-49)].



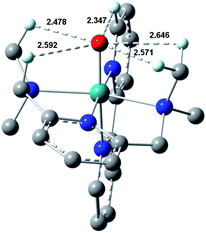
**Chart 6**

**Table 2.** Summary of redox potentials and kinetics of O2 evolution for complexes **8c**, **24a-c** and **25a-c**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| WOC | ***E1/2*III/II (V)** | ***E1/2*IV/III (V)** | ***E1/2*O2 (V)** | **IRa**  **(μmol h-1)** | **TONb** |
| 8c | 0.81 | 1.12 | 1.29 | 26 | 310 |
| 24a | 0.55 | 0.90 | 1.40 | 0.89 | 148 |
| 24b | 0.48 | 0.85 | 1.37 | 1.1 | 173 |
| 24c | 0.42 | 0.80 | 1.30 | 2.2 | 251 |
| 25a | 0.68 | 1.15 | 1.29 | 3.1 | 123 |
| 25b | 0.63 | 0.98 | 1.27 | 4.2 | 184 |
| 25c | 0.58 | 0.93 | 1.23 | 5.2 | 253 |

Data taken from refs [47] and [48]. Potentials *E1/2*vs. SCE; aIR is the initial rate of O2 evolution; bTON = catalytic turnovers after 40 h.

Another example is the tridentate ligand bound in complex **26** with two robust *σ*-donating tertiary amine groups [32,[[50]](#endnote-50)]. Coordinated amine groups have a significant influence not only on lowering the redox potentials but also on increasing the p*Ka* value of RuIII/II which, in turn, affects the pH-dependent redox potential of the RuIII/II couple. In addition, the rich *σ*-donating electronic environment also makes higher oxidation states of the complex more stable; diffraction quality monocrystals of the [RuIV=O]2+ complex were even grown at 4 °C. The optimized crystal structure (Figure 1) shows that hydrogen bonding exists between the oxido ligand and the H atoms of the methyl and methylene moieties of the tertiary amine ligand as well as one pyridyl C―H. The positive influence of H-bonding on stabilizing high-valent [RuIV=O]2+ species, however, results in its reduced reactivity. Regarding reaction rates, the rate constant of *kIV-V* for oxidation of [RuIV=O]2+ to [RuV=O]3+ is markedly smaller than *kO-O* for the reaction of [RuV=O]3+ with water. Thereby, the WNA reaction is favored by the [RuV=O]3+ instead of [RuIV=O]2+. In particular, the lack of reactivity in WNA seen for [RuIV=O]2+ probably arises from predicted high energy barriers [[[51]](#endnote-51),[[52]](#endnote-52)]. In order to overcome this problem, ligand modification can be considered to reduce the barrier of WNA and further improve the catalytic activity for water oxidation. One possibility is to increase the electrophilicity of the [RuV=O]3+ species by ligand fluorination; another option is to modify the NNN-ligand with a basic functional group to facilitate water deprotonation [50]. For O2 evolution during water oxidation by complex **26**, TON and TOF were measured as 4.6 and 1.03×10-3 s-1, respectively. The reason for the determined low TON value can be deactivation of the water oxidation capacity of the catalyst by associated oxidation processes, caused by the strong Ce(IV) oxidant.



**Figure 1.** Calculated crystal structure of the [RuIV=O]2+ species **26** showing H―bonding of the oxido ligand. Reprinted with permission from ref. [50]. Copyright (2012) The Royal Society of Chemistry.

We have mentioned previously that anionic tridentate ligands in complexes **6** and **7** are able to lower the oxidation potentials when forming the higher oxidation states. However, the anionic tridentate ligand seems to play further functional roles and impacts much of the catalytic cycle in contrast to the neutral tridentate tpy ligand in the [Ru(NNN)(NN)(H2O)] complex. Sun et al. [[[53]](#endnote-53)] summarized the advantages of introducing an anionic carboxylate ligand to complex **27** (Chart 6). These include facilitating catalytic water oxidation by lowering the overpotential, reducing the barrier to the release of O2 and attracting H2O to the reactive Ru metal center by possible H-bonding with the water molecules. The WNA mechanism of water oxidation was proposed to occur for this WOC through the catalytic cycle [RuII―OH2]+ → [RuIII―OH2]2+ → [RuIV=O]+ → [RuV=O]2+ → [RuIII―OOH]+ → [RuIV―OO]2+ → [RuII―OH2]+. In particular, the lone pair donated by the carboxylate group to the high-valent Ru center via p*π*―d*π* interaction may enable extraction of electrons from the metal center, but suppresses the release of a proton. Consequently, complex **27** thus favors the ET pathway rather than the PCET process. The TON and TOF values for the O2 evolution by this complex were determined to be 540 and 0.165 s-1, respectively. The TON value was measured after merely 1 h of the reaction time because of deactivation caused by decomposition. The TOF value was significantly higher than those observed for **8c** and its derivatives (Table 1); it is also ca. eight times higher than the overall catalytic rate constant (*kcat* = 2×10-2 s-1), thus suggesting that the WNA catalytic pathway is accompanied by another unobserved but more competitive water oxidation pathway, as TOF is typically about one quarter of the *kcat* value. The critical step of the WNA is defined as the formation of the O―O bond and the rate of this step closely correlates with *kcat*. On the other hand, the WNA reaction can be slowed down by reduced electrophilicity of the high-valent species when the electron density at the metal center increases. Thus, the overall catalytic rate can be compromised in this case. Interestingly, the lower activity in the Ru(V) oxidation state can be improved by association with protons and the assistance of hydrogen bonding between the carbonyl group and the incoming water, resulting in a fairly high reaction rate [53].

In another example, both tpy and bpy ligands can be replaced by tris(2-pyridylmethyl)amine (TPA) derivatives that have four π-acceptors (polypyridyl groups) and one σ–donor (a tertiary amino group), providing thermodynamic stability for complexes formed by its pentadentate chelation [[[54]](#endnote-54)]. As catalysts, metal complexes with the TPA ligand are attractive because their stable high oxidation states can be accessed through a PCET process both experimentally and by theoretical investigations [[[55]](#endnote-55),[[56]](#endnote-56),[[57]](#endnote-57)]. Bearing these advantages in mind, Zhao and co-workers prepared a series of mononuclear Ru complexes with TPA-based ligands and reported their activity for water oxidation (Chart 7, **28-31**) [[[58]](#endnote-58),[[59]](#endnote-59)]. A descending trend of catalytic activity and stability for water oxidation by these complexes has been reported: **28** > **29** ≈ **30** ≈ **31**. The enhanced activity of **28** is due to the introduction of a bpy moiety in the pentadentate species. Complex **28** is likely to follow a mononuclear reaction pathway as encountered for **8b**. However, the formation of a binuclear species along the reaction pathway is observed for complex **29**, being responsible for the lower activity due to the non-covalent π-π interaction between the isoquinoline substituents, which blocks the O―O bond formation. Bis(aqua) complexes **30** and **31** exhibit catalytic activities very similar to that of another bis(aqua) complex **32** [[[60]](#endnote-60)]. As reported by Llobet et al. [[[61]](#endnote-61)], decomposition of methylenic units in octadentate tetranucleating ligands (viz. 3,5-dipyridyl-pyrazoles linked by a xylyl group attached at the pyrazolate moiety) to CO2 may deactivate Ru catalysts. Based on experimental observations, production of CO2 can take place during water oxidation, particularly by complexes **28**, **30** and **31**. Compared to the modified pentadentate TPA ligand in complex **28** (O2 formation is about twelve times faster than CO2 formation), the methylenic groups in the less stable tetradentate TPA ligands of **30** (*k*O2 ~ 1.5×*kCO2)* and **31** (*kCO2* ~ 1.7×*k*O2) seem to be much more easily oxidised to CO2. The low catalytic activity of **30** and **31** can thus be rationalized by the accompanying catalyst decomposition from simultaneous oxidation of the ligand to generate CO2.

**Chart 7**

Complex **32** (*cis*-[RuII(bpy)2(H2O)2]2+, Chart 7) containing two aqua-ligands ideally leads to four PCET processes producing the high-valent bis(oxido) complex *cis*-[RuVI(bpy)2(O)2]2+ [[[62]](#endnote-62),[[63]](#endnote-63)]. For water oxidation, only the cis complex is identified to catalytically produce dioxygen and neither the cis → trans isomerization process nor the ligand-loss process for generating RuO2 are the rate determining steps. The π system of the catalytically active bis(oxido) state has unpaired spin density on both the Ru and O atoms and favors the WNA reaction in the aqueous solution with a relatively low activation free energy. However, intramolecular O―O bond formation is not supposed to occur along the catalytic pathway because of high activation free energy when driving together the two O σ lone pairs of electrons [60]. Therefore, the WNA pathway for water oxidation by the catalytically active “bis(oxido)” complex formed from [RuII(bpy)2(H2O)2]2+ can be proposed, as shown in Scheme 4.



**Scheme 4.** Proposed pathways of water oxidation by catalytically active “bis(oxido)” form derived from complex **32**, [RuII(bpy)2(H2O)2]2+. Reproduced with permission from ref. [60]. Copyright (2010) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

*2.3. Ligand effects of mononuclear Ru aqua complexes on water oxidatio*n

In the preceding sections two series of mononuclear Ru aqua complexes have been introduced, focusing in particular on their performance in catalytic water oxidation. A pronounced impact on the catalytic activity can be observed by tuning the electronic properties of particular dominant and ancillary ligands (in general, tpy and bpy) with suitable electron-donating or electron-withdrawing substituents. For example, the catalytic activity of [Ru(tpy)(bpy-R)(H2O)]2+ can generally be favored by electron-donating substituents or disfavored by electron-withdrawing groups. Here, we may conclude how the electron-withdrawing and electron-donating properties of ligands (tridentate and bidentate) influence the catalytic activity for water oxidation by employing different ligands containing pyridine rings with a higher nitrogen content, saturated amino groups (Ru―N coordination), phenolic or carboxylate moieties (a Ru―O bond) or carbenes (a Ru―C bond). Based on studies of the selected examples, it appears that electron-withdrawing ancillary ligands result in a high catalytic activity towards water oxidation and, in contrast, dominant ligands with different electronic properties play more complicated roles in selective stabilization or destabilization of oxidized species in each catalytic step. For example, with regard to a complex containing an electron acceptor ligand, its replacement with an electron donor ligand increases the driving force of electron transfer by reducing oxidation potentials and stabilizing high-valence states of the complex. However, it may have a negative impact on the WNA reaction, which favors electron-withdrawing ligands that decrease the energies of the lowest unoccupied molecular orbitals (LUMO) localized on the Ru―O bond, and the driving force of the O2-evolving oxidation. Therefore, the variation of the dominant ligands also becomes one of the factors considered to impact on the performance of the water oxidation catalysts. However, the positive influence of a ligand type on the activity is generally only addressed in specific catalytic processes rather than on the overall performance of the whole catalytic cycle. Moreover, perturbations may result from side effects including oxidant concentration, pH, solubility, decomposition and competitive oxidation. The competing roles and combined external effects preclude a clear correlation between electronic properties of ligands and catalytic activity to be drawn.

As mentioned, only trans aqua isomers are available as catalysts for water oxidation, so another ligand aspect impacting catalytic activity is thus the trans-cis effect. From computational studies [49], the structures of high-oxidation states of *trans*-**8d**, *cis*-**8d** and **8c** (Figure 2) show that the length of Ru―C bond is 1.99 Å in **8d′**, but when an *N*-heterocyclic carbene ligand is trans coordinating to the O2 binding site this bond is much shorter in comparison to the cis Ru―C bond (2.03 Å) and the *t*rans Ru―N bonds in **8d″** (2.09 Å) and **8c′** (2.09 Å). This indicates that trans Ru―C bonding is much stronger and makes the thermodynamics of O2 release from the singlet end-on conformation more exothermic by as much as 14.4 kcal mol-1 for **8d″** and 16.2 kcal mol-1 for **8c′**. As a consequence, these results suggest a significant destabilization of the end-on O2 binding in the singlet state, which may cause the release of O2 to be more efficient.

**Figure 2.** The structures (bond lengths in Å) of [RuIV-(OO)]2+ high-oxidation states and O2 release thermodynamics of *trans*-**8d**, *cis*-**8d** and **8c**. Reproduced with permission from ref. [49]. Copyright (2013) American Chemical Society.

Beside the influence of substituents, ligand type and trans-cis effects, another important ligand influence on the WOC activity that should be underlined is the geometric arrangement of the aqua ligand. From experimental investigations (complexes **4-X**, **8c-X** and **33-43** in Table 3 and Charts 8 and 9), Thummel and co-workers suggested that mononuclear WOCs of the type [Ru(NNN)(N)2(X)] (e.g., **4**, **35** and **37**, Chart 8) are, in general, more active than [Ru(NNN)(NN)(X)] (such as **8c**, **34** and **36**, Chart 8), through the WNA mechanism and without the potential effect of oxidative decomposition [25]. In particular, the variable ligand, X, can be either H2O or halide as the pre-catalysts undergo halide-water exchange during an induction period. Furthermore, a significant induction period (≥ 10 min) in the initial stage of the water oxidation may generate catalysts (for example, for **4-Cl**, **33a**, **38a** and **42**) at low initial rates. Here, the exceptional examples are the iodido complexes **4-I** and **8c-I**. As shown in Table 3, they exhibit remarkably higher (1610×10-4 s-1 for **4-I**) or at least comparable (190×10-4 s-1 for **8c-I**) initial rates of O2 evolution than their aqua-forms (370×10-4 s-1 and 190×10-4 s-1, respectively). These results reveal a different catalytic pathway that does not require an induction period, in contrast to the chlorido and bromido complexes.

**Chart 8**

**Table 3.** Summary of O2 evolution for complexes **4-X**, **8c-X**, and **34-43**.

|  |  |  |
| --- | --- | --- |
| WOC | **TOF( × 10-4 s-1)** | **TONa** |
| 4-OH2 | 370 | 300 |
| 4-Cl | 50 | 370 |
| 4-Br | 40 | 140 |
| 4-I | 1610 | 378 |
| 8c-OH2 | 190 | 270 |
| 8c-Cl | 20 | 390 |
| 8c-Br | 150 | 450 |
| 8c-I | 190 | 570 |
| 33a | 13 | 1170 |
| 33b | 280 | 1135 |
| 34 | 0 | 0 |
| 35 | 230 | 350 |
| 36 | 0 | 0 |
| 37 | 80 | 152 |
| 38a | 20 | 400 |
| 38b | 280 | 450 |
| 39a | 0 | 0 |
| 39b | 50 | 60 |
| 40 | 80 | 155 |
| 41 | 50 | 9 |
| 42 | 10 | 66 |
| 43 | 0 | 0 |

Data taken from ref. [25]. aTON = catalytic turnovers after 24 h.

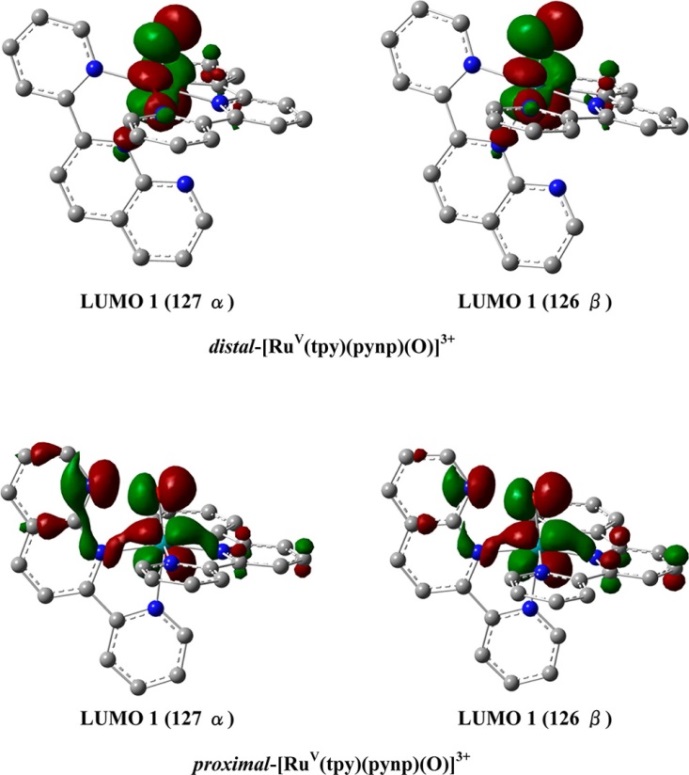
A similar effect of the geometric arrangement of the aqua ligand on the WOC is also observed for pre-catalyst couples **34/35** and **36/37** because they undergo the ligand conversion to the catalytically active aqua-species in the initial catalytic step. Complexes **35** and **37** show reasonable activity in water oxidation for the exchangeable ligand localized in the equatorial plane. By contrast, the activity is blocked when the exchangeable ligand is placed in the axial position in complexes **34** and **36**. Therefore, this evidence gives further credence to complexes of the type [Ru(NNN)(N)2(H2O)] regarding enhanced reactivity with water. Then another factor has to be considered in this case. By comparing the structures of tridentate ligands in these complexes, the reduced activity appears not only to be due to the position of the exchangeable ligand (either equatorial or axial), but also possibly arising from steric characteristics of the tridentate ligands. Complexes **35** and **37** contain a 2-pyridyl-phen and 8-quinolinyl analogue, respectively. In particular, the larger 5-membered chelate ring coordinating to the Ru center in complex **37** shows significant steric hindrance effect on the catalytic activity, causing a reduction in the TOF. In addition, the steric hindrance can be caused by the bidentate ligands. The bpy ligand is replaced by the 2-(pyrid-2′-yl)-1,8-naphthyridine (pynap) ligand in complexes **33a** and **33b**; this unique ligand combines stereochemistry with delocalization and electronegativity properties resulting in a most impressive stability (TON) rather than a catalytic activity (TOF) in this series of complexes. The effect of the pynap ligand will be discussed in detail in the following section.

In order to better understand the effect of steric hindrance on the catalytic performance, the phen ligand in **38** was modified to 2-methyl-phen (**40**) and 2,9-dimethyl-phen (**39**, Chart 9). Compared to **38a** (Table 3), the activity of Cl-complex **39a** is completely blocked by the 2,9-dimethyl-phen ligand, the two methyl groups also impact on the activity stability of the aqua form **39b** compared to complex **38b**, decreasing the TOF to 50×10-4 s-1 and the TON to 60. Interestingly, the activity can be recovered and the stability can partly be mended when only one methyl group is attached to the phen ligand (**40**), giving a TOF of 80×10-4 s-1 and a moderate TON of 155. Moreover, the effect of steric hindrance is also observed for **41** and **42** (Chart 9) where an extra benzene ring is fused onto the bpy ligand to increase steric crowding due to H8 being close to the metal center. As shown in Table 3, the catalytic activity of both **41** (TOF = 50×10-4 s-1) and **42** (TOF = 10×10-4 s-1) is reduced by the extra ring compared to that **8c-OH2** (TOF = 190×10-4 s-1). This effect is more pronounced for **42** where the ring is proximal to the chloride ligand. Furthermore, the activity is fully suppressed due to a more significant steric hindrance effect when the bpy ligand is extended by two phenyl rings, forming 2,2′-biquinoline as in complex **43**.

**Chart 9**

As discussed in the preceding text, the pynap ligand in complex **33** plays an important role in promoting catalytic water oxidation rather than imposing a negative effect due to steric hindrance. The pendant nitrogen lone pair base of the uncomplexed naphthyridine triggers PCET reactions with low activation barriers [[[64]](#endnote-64),[[65]](#endnote-65)], which are critical processes for water oxidation, leading to mitigation of charge build-up and reduction of the overpotential [19,20,21]. To further investigate the function of this pendant base in water oxidation, two isomers of *distal*-[Ru(tpy)(pynap)(H2O)]2+ and *proximal*-[Ru(tpy)(pynap)-(H2O)]2+ isomers were prepared by Thummel and Fujita et al. (**44** and **45**, Chart 10) [[[66]](#endnote-66)]. Isomers **44** and **45** showed lower metal-centered oxidation potentials as induced by the pendant bases. The initial oxidation process for **44** is a two-step reaction including one PCET process producing [RuIII–OH]2+ from [RuII–OH2]2+ and one ET reaction, oxidizing [RuIII–OH]2+ further to [RuIV=O]+ over a particular pH range. By contrast, isomer **45** undergoes a single-step reaction comprising two PCET processes forming the [RuIV=O]+ species. Notably, the initial oxidation potential of **45** (1.11 V vs. SCE in acetone) is higher than that of **44** (1.06 V) measured under the same conditions, suggesting a H-bonding interaction between the aqua ligand and the pendant base in **45**.

Water oxidation through the WNA reaction was also evaluated for isomers **44** and **45**. The involvement of the pendant base in **44** resulted in significantly increased stability in terms of TON reaching more than 3200 after 48 h, with TOF of 1.8×10-2 s-1, while a low TON value of 460 was determined for **8c** at the same time, with TOF of 19×10-3 s-1. Surprisingly, isomer **45** provided very low TOF of 1.1×10-3 s-1 and TON of approximately 1. The poor water oxidation activity and stability in the latter case can be accounted for by ligand decomposition, as deduced from the evolution of carbon dioxide during the catalytic process. Similar observations on redox properties and water oxidation activity of **44** and **45** have been reported by Yagi and co-workers, [[[67]](#endnote-67)] who also noticed photoisomerization of **44** to **45**. Furthermore, they described ligand decomposition in *proximal-*isomer **45** probably due to delocalisation of the LUMO [[[68]](#endnote-68)]. As displayed in Figure 3, the dominant LUMO is localised on the [Ru=O] unit in the oxidised form [RuV=O]3+ of *distal*-isomer **44**, leading to a better overlap with the nucleophilic water lone pair orbital, further improving the formation of the O―O bond in the WNA step. Conversely, the LUMO of the *proximal*-[RuV=O]3+ oxidation state of **45** is extended over the pynap ligand, making it difficult to form the O―O bond as a consequence of the higher free energy of activation for *proximal*-[RuV=O]3+ (Δ*G*‡ = 87.9 kJ mol-1) in comparison with *distal*-[RuV=O]3+ (Δ*G*‡ = 104.6 kJ mol-1).



**Figure 3.** LUMOs of the [RuV=O]3+ redox form of *distal*-isomer **44** (top) and *proximal*-isomer **45** (bottom). Reprinted with permission from ref. [68]. Copyright (2013) American Chemical Society.

Due to the ligand decomposition during WOC, isomer **45** did not provide any valuable evidence for H-bonding itself affecting the catalytic activity. In order to ascertain this, Llobet and co-workers prepared two isomers with fluoro substituents on the bpy ligand, viz. **46** and **47** (Chart 10). H-bonding was then observed between the fluoro substituent and the aqua ligand in **47** as judged from its X-ray structure [[[69]](#endnote-69)]. According to the H-bonding situation, the p*Ka* value of **47** is much higher than that of **46**, indicating that a more basic environment can be generated by isomer **47** to stabilize the [RuII―OH]2+ species. However, the oxidation potentials for both isomers are identical, suggesting that both isomers experience the same electronic effect on the Ru metal center in spite of the different positions of the fluoro substituents on the bpy ligand. Therefore, differences in the WOC activity between isomers **46** and **47** can be ascribed to the influence of H-bonding. The values of TOF = 1.7×10-3 s-1 for H-bonding isomer **47** are approximately two times lower than those obtained from the non-H-bonding isomer **46**. This observation can probably be attributed to a potential stabilisation of the [RuIII‒OOH]+ intermediate through the H-bonding between Ru―OOH and the nearby fluoro substituent. The stabilization would markedly slow down the process of O2 release, which corresponds with the increased basicity, compared to **47**, along the initial PCET process. This conclusion has been supported by theoretical studies of the water oxidation by complexes **1b** and **4**. These studies have revealed that the unique H-bonding in **1b** stabilizes the peroxide species [RuIII―OOH]2+ by a few kcal mol-1 and allows the O2 release to be more exothermic than in the case of **4** [49].



**Chart 10**

**3. Mononuclear Ru non-aqua complexes for water oxidation**

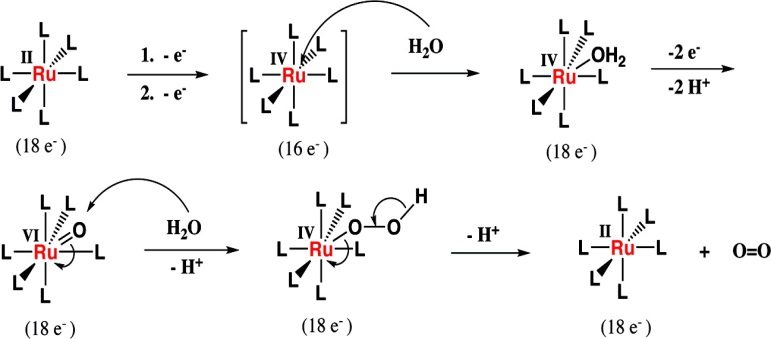
*3.1. Ruthenium complexes with pyridine-type ligands*

As commented above, the equatorial ligand 2,9-dipyrid-2′-yl-1,10-phenanthroline (dpp) in fact favors tetradentate binding to the metal center due to substantial distortion, thus forming a species (**5′a**, Chart 11) that only contains pyridine-type ligands (with two axial 4-picolines) and not the equatorial aqua ligand proposed for **5** (Chart 2). The dpp ligand incorporates phen as the internal subunit to provide thermodynamically stable complexes due to its tetradentate chelation and to avoid conformational mobility around the central C―C bond [[[70]](#endnote-70)], alike the bpy backbone that is prone to photochemical or thermal conversion between the trans isomer and the more stable chelated cis geometry [[[71]](#endnote-71)]. Thummel and co-workers reported a series of equatorial tetradentate ligands in mononuclear Ru complexes (**5′a-c** and **48-51**, Chart 11). They all exhibit reasonable WOC performance in terms of TON values under the same catalytic conditions; information about TOF has not been provided in this specific case [23]. For complex **5′a** TON = 416 was observed. The low TON value of 186 achieved by **5′c** has been ascribed once more to protonation of the dimethylamino substituents under acidic conditions, causing them to function as electron-withdrawing groups. On the other hand, the negative influence of the tetradentate ligand in these complexes on the catalytic performance can be ascribed to their steric bulk preventing a substrate from entering the coordination sphere of the Ru center in high oxidation states. The catalytic performance of **49** (TON = 384) and **51** (TON = 396) is comparable to that of **5′a**, suggesting that the additional pyridyl rings are not detrimental, whereas the extended rings in **50** may introduce a steric hindrance effect onto the catalytic performance (**50a**: TON = 148, **50b**: TON = 213). It is thus of utmost importance to understand the mechanism of water oxidation by this kind of complexes.



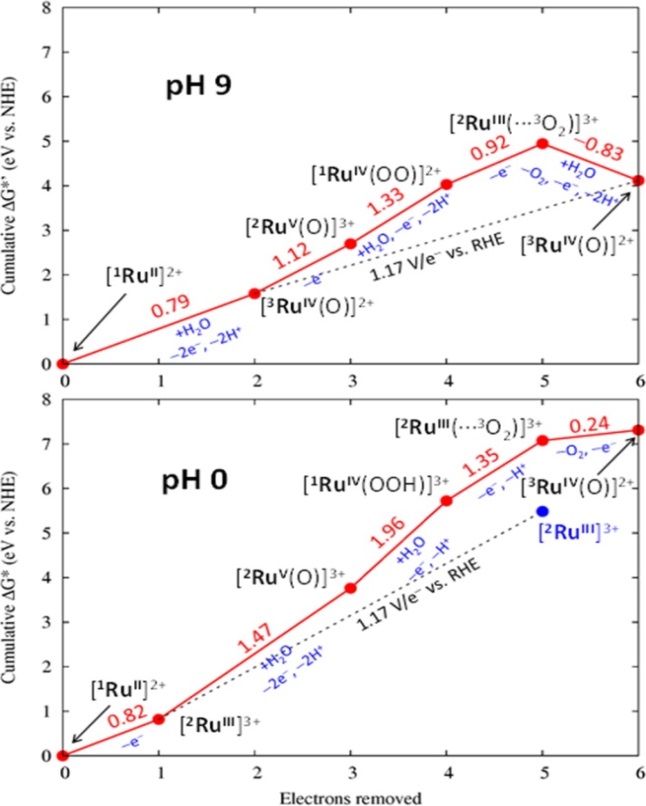
**Chart 11**

The likely catalytic cycle of **5′a** has been established by density functional theory (DFT) calculations [24]. As displayed in Scheme 5, a water molecule is able to coordinate to the 16-electron Ru(IV) center at a seventh site in the equatorial plane, forming a seven-coordinate aqua species after two-electron oxidation of the 18-electron initial form **5′a**. The new 18-electron species, [RuIV―OH2]4+, is probably a high-spin (triplet) intermediate since the binding energy to H2O of the triplet form is lower by 6 kcal mol-1 than that of the low-spin (singlet) complex. Next, the [RuIV―OH2]4+ species is converted to the 18-electron triplet [RuVI=O]4+ by a two-PCET process and then to [RuIV―OOH]3+ by a WNA reaction.



**Scheme 5.** Proposed catalytic cycle of water oxidation by catalyst **5′a**. Reprinted with permission from ref. [24]. Copyright (2008) American Chemical Society.

More recently, combining electrochemical and spectroscopic experimental studies with theoretical analysis of the energetics, thermochemistry and spectroscopic properties of intermediates, a pH-dependent catalytic mechanism through seven-coordinate intermediates for water oxidation by the reference complex **5′a** was suggested by Muckerman and co-workers to complement the previous proposal [[[72]](#endnote-72)]. At low pH (pH =0, Figure 4 (bottom)), the catalyst [RuII]2+ is initially oxidised to [RuIII]3+ that energetically favors two PECT processes with H2O resulting in the seven-coordinate species [RuV(O)]3+. Subsequently, [RuV=O]3+ undergoes a PECT reaction with another water molecule to form the O―O bond in a hydroperoxido species [RuIV―OOH]3+. In the next O2 release step, the weakly bound [RuIII(…O2)]3+ is generated by a PCET reaction of [RuIV―OOH]3+ followed by spin pairing. Consequently, the dissociation of O2 is significantly slowed. Therefore, another oxidation process to release O2 would be necessary for [RuIII(…O2)]3+ to produce [RuIV]4+, which immediately couples with a water molecule through a 1e-/2H+ PCET process to give [RuIV=O]2+ involved in the catalytic cycle. In contrast, the catalyst [RuII]2+ undergoes an energetically favorable reaction with H2O through a 2e-/2H+ PECT process to produce the seven-coordinate intermediate [RuIV=O]3+ under basic conditions (pH 9, Figure 4 top). [RuIV=O]3+ is further oxidised to [RuV=O]3+ followed by a 1e-/2H+ PCET oxidation with H2O to give an 18-electron singlet peroxido species [RuIV―OO]2+. The remaining processes in the catalytic cycle are comparable to those observed under the low pH condition. In particular, the same O2 evolution initiator [RuIII(…O2)]3+ can be produced by an electron transfer reaction of [RuIV―OO]2+.



**Figure 4.** Latimer-Frost diagrams for the theoretical investigation of catalytic water oxidation by complex **5′a** at pH 9 (top) and pH 0 (bottom). Reprinted with permission from ref. [72]. Copyright (2014) American Chemical Society.

In search for all-pyridine containing complexes suited for catalytic water oxidation, representatives based on homoleptic [Ru(bpy)3]2+ (e.g., [Ru(bpy)2(pic)2]2+, [Ru(bpy)(pic)4]2+) and [Ru(tpy)2]2+ (e.g., [Ru(tpy)(bpy)(pic)]2+, [Ru(tpy)(pic)3]2+) were prepared. However, only [Ru(tpy)(bpy)(pic)]2+ and [Ru(tpy)(pic)3]2+ exhibited a moderate catalytic performance characterized by TON of 95 and 135, respectively; no TOF values have been reported.[24] The kinetics of O2 evolution with [Ru(tpy)(bpy)(pic)]2+ and [Ru(tpy)(pic)3]2+ is very similar to that observed for a commercial sample of RuO2. Catalyst decomposition is thus assumed to occur, both complexes being oxidized to the more active heterogeneous water oxidation catalyst RuO2 [[[73]](#endnote-73),[[74]](#endnote-74)]. Further mechanistic studies of [Ru(tpy)(pic)3]2+ were carried out by Sun and co-workers who suggested that the Ru-aqua species is the actual catalyst produced by replacement of the pic ligand with water [[[75]](#endnote-75)]. On the other hand, the tpy ligands in [Ru(tpy)2]2+ occupying all equatorial and axial sites may be responsible for the catalytic inactivity of this complex in water oxidation due to steric strain effects. Firstly, one of the tpy ligand in [Ru(tpy)2]2+ in the arbitrarily defined equatorial plane lacks sufficient angle strain, impeding the attack of a water molecule in this plane. Secondly, the other tpy ligand is not able to provide a nearly linear axial arrangement required by the formation of a heptacoordinate pentagonal bipyramid, thereby making the formation of the prerequisite seven-coordinate geometry impossible [[[76]](#endnote-76)]. This problem can be overcome by employing the 2-(quinol-8′-yl)-1,10-phenanthroline (phenq) ligand [[[77]](#endnote-77)] to produce the heteroleptic complex [Ru(phenq)(tpy)]2+. The increased size of phenq by the two fused extra rings results in significant geometry changes. The nearly linear geometry of the axial ligand arrangement and the large dihedral angle make the complex more amenable to form seven-coordinate geometry complexes and thus more active for water oxidation.

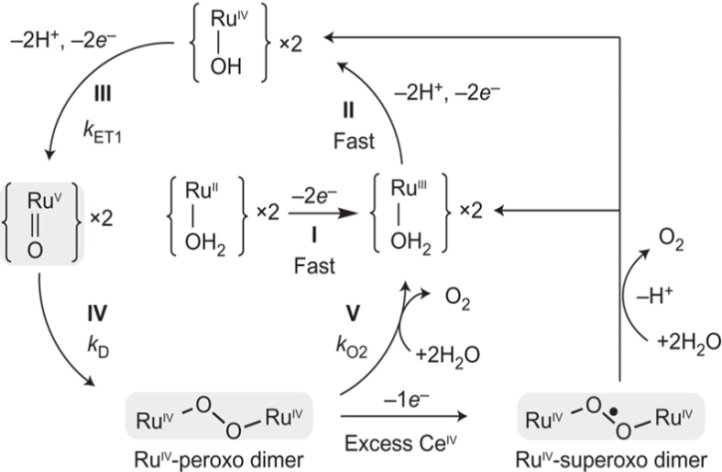
*3.2. Ruthenium complexes with anionic ligands*

It has been a great challenge to isolate the high-valent intermediates in the discussed Ru-based catalytic cycles due to their instability. Any success in this strategy can no doubt be very helpful for understanding the mechanism of the catalytic water oxidation process. Sun and co-workers [[[78]](#endnote-78)] used the dianionic ligand 2,2′-bipyridine-6,6′-dicarboxylic acid (bda) to prepare the neutral mononuclear Ru WOC, [Ru(bda)(pic)2] (**52**, Chart 12) that shows an excellent catalytic performance in both thermal and visible light-driven water oxidation [[[79]](#endnote-79),[[80]](#endnote-80)]. The strong electron donating ability of the carboxylate ligands stabilizes the higher oxidation states of the metal center [[[81]](#endnote-81)], making isolation of high valence intermediates possible. By mass spectrometry, two isolated oxidation states were identified as **52a** and **52b** (Chart 12). Specifically, **52b** contains hydroxyl as the seventh ligand which may originate from a water molecule bound in the seventh coordination position at the Ru center when dissolving complex **52** in an aqueous solution. This assumption is supported by computational studies showing that the water coordination in the Ru(II) state is in line with a large O―Ru―O angle in the equatorial plane and extended axial Ru―N bonds [[[82]](#endnote-82),[[83]](#endnote-83)]. The initial steps of the water oxidation mechanism can thus be described as [RuII―OH2] → [RuIII―OH2]+ → [RuIV―OH]+ (Scheme 6). Interestingly, X-ray analysis reveals that the crystal structure of **52b** actually consists of two [RuIV] units connected by a hydrogen bonding network [HOHOH] responsible for a unique bridged structure with two seven-coordinate Ru centers (**52c**, Chart 12) [78]. This dinuclear intermediate is also active in water oxidation. The O―O bond formation step is thought to be triggered by two PECT oxidation processes to form [RuIVOH(-), •ORuIV]4+ transforming to [RuIVOH•, •ORuIV]5+. The latter species then undergoes a radical coupling dimerization reaction resulting in the formation of the O―O bond [82].



**Chart 12**

Kinetic analysis conducted under stoichiometric conditions indicates that the monomeric [RuV=O]+ species formed from [RuIV―OH]+ by the PCET oxidations is in fact the active intermediate which further converts to a radical complex undergoing the radical coupling dimerization [83]. The O―O bond thus results from an interaction of two radical M―O units (I2M pathway) rather than a WNA pathway. The dimerization process is fast and produces the peroxido dimer (Scheme 6) featuring a low-spin antiferromagnetic configuration [82]. In the O2 release step, the peroxido dimer reacts with two water molecules to generate O2 and reintroduce the [RuIII―OH2]+ species into the catalytic cycle. Scheme 6 also features the catalytic path with an excess of Ce(IV) oxidizing the peroxido dimer to a triplet superoxido dimer with a low-spin ferromagnetic configuration followed by O2 evolution and formation of the [RuIII―OH2]+ and [RuIV―OH]+ species re-entering the catalytic cycle.



**Scheme 6.** Proposed catalytic cycle for water oxidation by catalyst **52**. Reprinted with permission from ref. [83]. Copyright (2012) Nature Publishing Group.

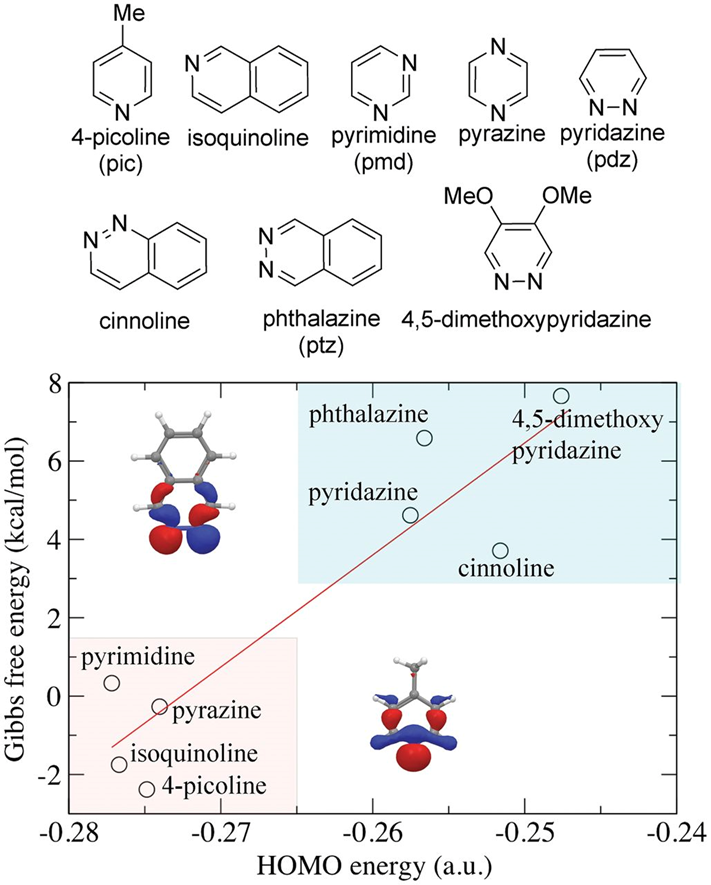
Non-aqueous mononuclear Ru complexes **5′a** and **52** containing a tetradentate ligand, however, feature totally different catalytic mechanisms towards water oxidation, in particular for the O―O bond formation step, resulting in different catalytic activity. The catalytic mechanism for **5′a** regards to water nucleophilic attack (WNA) route and for **52** it involves interaction of two M‒O units (I2M route). Based on the structures of these two complexes, the only difference is due to the coordinating tetradentate ligands and thus the ligand effect is the key to the O―O bond formation. From computational studies, Chen and co-workers suggested three factors induced by the tetradentate ligand on the activation barrier of the O―O bond formation in both mechanisms [[[84]](#endnote-84)]. First, the tetradentate ligand containing a phenyl or carbene group can lead the Ru complex to favor the WNA route towards the O―O bond formation since a *cis*-structure is usually preferred by the phenyl or carbene group with regard to a proton-accepting fragment. Thus, lowering the WNA reaction barrier is most likely a consequence of increasing the basicity of the proton-accepting group. Second, a catalyst with a more positive net charge seems to facilitate the WNA reaction by lowering the O―O bond formation barrier. By contrast, coulombic repulsion effects on the barrier in the I2M mechanism only arise when the net charge of the catalyst reaches 3+. Finally, the reaction barrier for the I2M mechanism is affected by the steric hindrance of the bulky ligand that inhibits formation of the seven-coordinate dimer.

High TOF of 4.5 s-1 and TON of 1200 were observed for WOC **52** (3.3 × 10-5 M). However, this complex lost its catalytic activity after merely 5 min by a degradation process involving axial ligand dissociation. In order to achieve higher stability and catalytic activity, modifications were performed on both equatorial tetradentate and axial monodentate ligands, resulting in significant improvements. In the first example, the bda ligand was replaced by the 1,10-phenanthroline-2,9-dicarboxylate (pda) ligand. The resulting complex [Ru(pda)(pic)2] displayed a TOF of 1.102 s-1 and a TON of 310 after 6 h [[[85]](#endnote-85)]. Surprisingly, the difference in catalytic activity and stability between these two catalysts was not due to the small structural change between the bda and pda ligands but due to the different mechanisms; [Ru(bda)(pic)2] followed the I2M route but [Ru(pda)(pic)2] the concurrent WNA route. The explanation for this observation considers the activation barrier for the O―O bond formation and the geometry of the pda ligand. From modelling studies, the catalytic state of [RuV(pda)=O]+ bears a relatively lower barrier for the WNA reaction compared to I2M, favoring a WNA pathway. In addition, the cleft of the pda ligand is more rigid and larger than that of the bda ligand to hold the Ru(III) ion in resultant [RuIII―OOH] after the WNA reaction, therefore suggesting participation of an auxiliary COO- ligand in the proton reshuffle[[[86]](#endnote-86)].

Another attempt to influence the WOC activity was made by replacing the axial 4-picoline ligands with different 4-substituted pyridines L in [Ru(bda)L2] in order to tune their electron donating/withdrawing properties and hydrophobic/hydrophilic character. Investigations revealed that complexes with electron-withdrawing substituent groups on the axial pyridine ligands induced higher catalytic performance in term of TON in comparison with electron-donating substituents [[[87]](#endnote-87)]. This trend is in a good agreement with the observations summarized in the preceding section.

The axial 4-picoline ligands can also be replaced by IMBr (5-bromo-*N*-methylimidazole))/IMBr or IMBr/DMSO (dimethyl sulfoxide) [[[88]](#endnote-88)], *N*-heterocyclic carbene/H2O [[[89]](#endnote-89)], and isoquinoline/isoquinoline [83], pyrimidine/pyrimidine, pyridazine/pyridazine, phthalazine/phthalazine [[[90]](#endnote-90)] combinations which have less or more electron-donating capacity in comparison with 4-picoline, respectively. Compared to the complex with IMBr/IMBr axial ligands, the complex containing the IMBr/DMSO axial ligand combination showed a higher catalytic activity. The main factor responsible for this difference does not seem to relate to the electronic properties of DMSO; rather, the DMSO ligand exhibits strong flexibility to reduce steric collisions during the transition state in the radical coupling dimerization (I2M) by the switch from the RuII―S to the RuIV―O coordination (linkage isomerism). However, the stability of this complex during the catalytic cycle is still not satisfactory.

In line with the Gibbs free energy of axial ligand exchange reactions, the correlation between the HOMO energy of ligands (Figure 5, top) and their stability was established (Figure 5, bottom) [90]. This work revealed that Ru‒bda complexes with axial ligands that feature higher HOMO energy, e.g., cinnoline, pyridazine, phthalazine and 4,5-dimethoxypyridazine, should be notably more stable than complexes with less electron-donating ligands such as pyrimidine, pyrazine, isoquinoline, 4-picoline. The higher stability, in terms of enhanced catalytic performance towards water oxidation, has been consistent with results of experimental studies. Under the same catalytic conditions (2.2 × 10-4 M catalyst), [Ru(bda)(pyridazine)2] with the robust pyridazine ligand showed TON of 4573 and TOF of ca. 31 s-1. It was deactivated in more than 1.3 h compared to less stable ligand system in [Ru(bda)(pic)2] (TON ~935 and TOF ~300 s-1 [83], deactivation in ca. 1.1 h) and [Ru(bda)(pyrimidine)2] (TON ~401 and TOF ~70 s-1, deactivation in ca. 0.3 h). Specifically, the complex bearing the less electron-donating isoquinoline ligand has a short catalytically active life, similar to the complexes [Ru(bda)(pic)2] and [Ru(bda)(pyrimidine)2]; however, it is more active than these two complexes as a consequence of non-covalent π―π stacking between isoquinolines of two different catalytic units during the I2M dimerization process [83]. The best catalytic performance was gained from [Ru(bda)(phthalazine)2], where the phthalazine ligand is far more robust than the ligands mentioned above. The catalytic process thus continued for more than 3 h and showed a remarkably large TON of ca. 55000 and TOF of ca. 286 s-1. Of note, the TON and TOF not only come from the effect of the stable phthalazine ligand, but also benefit from π-π stacking interactions, consistent with the similar observation made for [Ru(bda)(isoquinoline)2] [90]. In conclusion, the axial ligand effect can be clarified in terms of electronic properties. Quite simply, complexes binding more electron-donating axial ancillary ligands will be more active in water oxidation.



**Figure 5.** The series of axial ligands used for Gibbs free energy calculations (top) and the correlation between the Gibbs free energy for a ligand exchange reaction in an aqueous solution at pH 0 and *T* = 298 K, and the HOMO energy of the ligand (bottom). The inset shows the calculated HOMO and HOMO-1 of 4-picoline and phthalazine, respectively. Reprinted with permission from ref. [90]. Copyright (2012) National Academy of Sciences of the United States of America.

Interestingly, the I2M catalytic mechanism of Ru-bda complexes can be totally hindered when a water molecule occupies an axial coordination site, introducing the WNA reaction pathway instead [89]. This ligand effect can be assigned to electronic properties of the aqua ligand, causing much weaker interaction between two molecules of intermediate [RuV=O]+ reflected in a poor SOMO-SOMO overlap, thereby making the I2M coupling impossible (cf. Scheme 6). Furthermore, the low catalytic activity and stability (TOF = 0.04 s-1, TON = 63) shown by the Ru‒bda aqua complex suggests that the WNA reaction of the seven-coordinate [RuV=O]+ intermediate is much less efficient than the I2M coupling reaction.

In addition, Sun and co-workers reported a series of mononuclear Ru WOCs that contained a tridentate carboxylate ligand and the rest of the coordination sites were occupied by three pyridine-type ligands [[[91]](#endnote-91),[[92]](#endnote-92),[[93]](#endnote-93),[[94]](#endnote-94)]. These complexes undergo ligand exchange in an aqueous solution to produce aqua complexes with water replacing one pic ligand. Therefore, the WNA mechanism is probably favored for water oxidation by these WOCs.

**4. Conclusions**

This review deals with two principal families of water oxidation catalysts, that is aqua and non-aqua mononuclear ruthenium complexes containing tetradentate or tridentate primary ligands and monodentate or bidentate ancillary ligands. In particular, it pursues the influence of the ligands on the catalytic activity, including electronic effects given by the ligand nature and substituents, the trans-cis effect, steric hindrance and the strain effect, the net charge effect, the geometric arrangement of the aqua ligand and the intraligand interaction factors such as hydrogen bonding or pendant base. Understanding the ligand role in the catalytic cycle should ideally provide an important guidance to develop in a predictable and rational manner more suitable ligands coordinating the Ru center to ensure higher catalytic activity towards water oxidation. However, one point should be initially addressed in that the role of the ligand effects is generally paradoxical towards catalytic activity since they may act as a promoter in certain catalytic steps and, in contrast, as an inhibitor in others. Ligand design for water oxidation catalysts should therefore be considered in order to balance positive and negative influences and to achieve the best performance in the rate determining catalytic step and improved overall activity along the whole catalytic cycle.

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