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Redox-Active Ligand Assisted Catalytic Water Oxidation by Ru(IV)=O Intermediate

Jing Shi,^[a] Yu-Hua Guo,^[a] Fei Xie,^[a] Qi-Fa Chen^[a] and Ming-Tian Zhang*^[a]

Abstract: Water splitting is one of the most promising solutions for storing solar energy in a chemical bond. Water oxidation is still the bottleneck step because of its inherent difficulty and the limited understanding of the O-O bond formation mechanism. Molecular catalysts provide a platform for understanding this process in depth and have received wide attention since the first Ru-based catalyst was reported in 1982. Ru(V)=O is considered a key intermediate to initiate the O-O bond formation via either a water nucleophilic attack (WNA) pathway or a bimolecular coupling (I2M) pathway. Here, we report a Ru-based catalyst that displays water oxidation reactivity with Ru(IV)=(O) with the help of a redox-active ligand at pH 7.0. The results of electrochemical studies and DFT calculations disclose that ligand oxidation could significantly improve the reactivity of Ru(IV)=O toward water oxidation. Under these conditions, sustained water oxidation catalysis occurs at reasonable rates with low overpotential (~ 183 mV).

Introduction

The sustainable production of clean energy is one of the greatest scientific challenges facing society's urgent energy demands.¹⁻⁴ The rational design of robust and efficient catalytic systems for splitting water into H₂ and O₂ is the most attractive way to address this problem because of its long-term potential of hydrogen as a clean, sustainable fuel.⁵⁻¹¹ Water oxidation (2H₂O \rightarrow O₂ + 4e⁻ + 4H⁺) involves a four-electrons and four-protons transfer process,¹²⁻¹³ which requires the catalyst to reach a high oxidation state and thus lessens the lifetime of high oxidation state intermediates, remains the challenge toward water splitting. Molecular catalysts provide a platform for an in-depth understanding of the mechanism of water oxidation, and studies on this mechanism will contribute to the development of the ideal catalysts.

Among the reported various molecular catalysts based on transition metals, such as Ru,¹⁴⁻²⁸ Ir,²⁹⁻³⁵ Mn,³⁶⁻⁴¹ Fe,⁴²⁻⁵¹ Ni,⁵²⁻⁵⁴ Co⁵⁵⁻⁶¹ and Cu,⁶²⁻⁶⁸ Ru-based catalysts have played an extremely important role in the development history of the field of water oxidation. The first molecular water oxidation catalyst (WOC), *cis,cis*-[(bpy)₂(H₂O)RuORu(OH₂)(bpy)₂]⁴⁺ (Blue dimer), developed by Meyer in 1982 inspired the continuous exploration on this field and the development of binuclear catalysts was a trend for a long time.⁶⁹ Based on an in-depth understanding of the

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Scheme 1. The structure of the catalyst, $[(L^{N5-})Ru^{III}-OH]^+$, investigated in this work.

catalytic mechanism of blue dimer, Llobet and his coworkers further developed the binuclear Ru catalyst using a linkage ligand to control the O-O bond formation.⁷⁰⁻⁷³ Interestingly, Thummel and Meyer found that binuclear design was not the only way, singlesite Ru is enough for water oxidation.^{21, 74}

Then water nucleophilic attack on Ru^V=O for O-O bond formation mechanism (WNA pathway) was first presented by Meyer and his coworkers.⁷⁴ This mechanistic study on O-O bond formation further deepened the understanding of the process of water oxidation and provided rational guidance for the design of a molecular water oxidation catalyst based on the types of transition metals. However, the required overpotential for Ru catalysts, such as [(tpy)(bpy)Ru^{II}-OH₂]²⁺, is quite high, because of the relatively high potential required for oxidizing Ru^{IV}=O to the desired intermediate Ru^V=O.75 Two strategies are applied for solving this problem: the first is introducing an electron-rich ligand, such as 2,2'-bipyridine-6,6'-dicarboxylate, presented by both the Sun and Llobet groups, to lower the oxidative potential of Ru^{IV}=O;^{18, 76} the second way, reported by Meyer, is using an electron-deficient ligand to improve the reactivity of Ru^{IV}=O and thus skip the formation of RuV=0.77 Interestingly, RuV=0 can react with hydroxide ion (OH⁻) with the help of the electron-deficient ligand and buffer at pH >11.6 although the rate is limited and almost absent of reactivity in a neutral solution to directly react with water. Despite that a Ru^{IV}=O mechanism would have the added advantage of a considerable decrease in overpotential for water oxidation, so far, how to improve the reactivity of Ru^{IV}=O to react with water is still a continuing problem.

High-valent iron-oxo complexes have been implicated as reactive intermediates in a range of biological transformations and in synthetic catalytic processes.⁷⁸⁻⁸⁵ Fe^{IV}-oxo porphyrin π -cation radical species, generated by porphyrin ligand oxidation and designated as Compound I (Cpd-I) in heme proteins (e.g., cytochrome P450), display a greater electrophilicity and oxidative reactivity than its one-electron-reduced analogue Fe^{IV}-oxo, designated as Compound II (Cpd-II), in heme enzymes.⁸⁶⁻⁸⁹ This shows that it is feasible to increase the water oxidation catalytic

RESEARCH ARTICLE

activity by $[(L^{N5-})^{++}Ru^{IV}=O)]^{2+}$ species. Herein, we report here that water oxidation does occur for a new family of $[(L^{N5-})^{++}Ru^{IV}=O)]^{2+}$ at pH 7.0 where L is a redox-active electron-rich polypyridyl ligand which is abbreviated as L^{N5-} (Scheme 1). The electrochemically generated $[(L^{N5-})^{++}Ru^{IV}=O)]^{2+}$ can sustain water oxidation catalysis at a reasonable rate with low overpotential (~ 183 mV) in neutral solution. The results of electrochemical studies and DFT calculations are in excellent agreement with each other and provide a mechanistic framework that addresses the influence of ligand oxidation on the enhancement of $Ru^{IV}=O$ toward water oxidation.

Results and Discussion

Synthesis and characterization of the catalyst, [(L^{N5-})Ru^{III}-OH]*. Owing to the accumulative electron-proton transfer involved in water oxidation, we developed an N5- ligand with an Nphenylacetamide fragment which can give an N⁻ coordination site with one unite of negative charge. This N⁵⁻ could serve as a redox reservoir during the multielectron catalysis, thus assisting the catalyst to reach a formal high valent state to react with water similar to the TAML-Co catalyst.⁹⁰ This ligand precursor (L^{N5H}) was prepared by crosslinking of carboxyl acid to the primary amine with DCC (dicyclohexylcarbodiimide) as a conjugation reagent (the details are listed in SI). When L^{N5H} was treated with Ru(DMSO)₄Cl₂ in DMF with microwave irradiation for 30 min, [(L^{N5-})Ru^{II}-CI] was isolated in 60% yield (Scheme 2). This complex was characterized by ¹H NMR and ESI-HRMS (See SI). The structure of [(L^{N5-})Ru^{II}-CI] was further verified by single-crystal Xray diffraction (Figure 1a). The structure displays as the typical distorted octahedral geometry around the Ru center, as expected for low-spin d⁶ Ru-(II). The ligand L^{N5-} coordinates with the Ru atom via its five N atoms and one CI anion that was in trans position to the amidate N-atom. Upon adding Ag⁺ into [(L^{N5-})Ru^{II}-CI] in water, the CI cannot be displaced but the complex was oxidized to [(L^{N5-})Ru^{III}-CI]⁺ with quantitative yield. This paramagnetic complex was confirmed by ESI-HRMS (Figure S6) and single-crystal X-ray diffraction (Figure 1b). Upon dissolving the obtained [(L^{N5-})Ru^{III}-Cl]⁺ in 0.1 M phosphate buffer (pH 7.0), the Cl⁻ was gradually displaced by OH⁻ with a rate constant of approximately $4.5 \times 10^{-4} \text{ s}^{-1}$ (Figure S7). Inspired by the above observation, we dissolved [(L^{N5-})Ru^{II}-CI] in 0.1 M phosphate buffer (pH 7.0) under air atmosphere and quantitatively obtained $[(L^{N5-})Ru^{III}-OH]^+$ with a rate constant of approximately $7.7 \times 10^{-4} \text{ s}^-$ ¹, indicating that it is a oxidative induced ligand exchange process. The obtained paramagnetic complex, [(L^{N5-})Ru^{III}-OH]⁺, displays similar geometry as the complexes [(L^{N5-})Ru^{II}-CI] and [(L^{N5-})Ru^{III}-Cl]⁺ except the Cl⁻ anion is replaced by OH⁻ anion (Figure 1c).



Scheme 2. Synthesis of the desired Ru complexes.



Figure 1. Solid-state structures of **[(L^{N5})Ru^{III}-CI]**, **[(L^{N5})Ru^{III}-CI]**⁺ and **[(L^{N5})Ru^{III}-N(4)**, 2.078(17); **Ru^{III}-N(4)**, 2.073(18); **Ru^{III}-N(5)**, 2.081(17); **Ru^{III}-N(1)**, 2.461(5); **RI^{III}-N(1)**, **I**¹-**R**^{III}, **I**¹-**R**^{III}, **I**¹-**R**^{III}, **R**^{III}, **R**^I

RESEARCH ARTICLE

Redox Properties of $[(L^{N5-})Ru^{III}-CI]^+$ **and** $[(L^{N5-})Ru^{III}-OH]^+$ **in propylene carbonate.** The redox properties of $[(L^{N5-})Ru^{III}-CI]^+$ in propylene carbonate recorded by cyclic voltammogram (CV) displays two reversible waves at -0.5 and 0.72 V vs Fc^{+/0} (Figure 2), corresponding to the successive oxidation of Ru^{II} to Ru^{III}, Ru^{III} to Ru^{IV}. For $[(L^{N5-})Ru^{III}-OH]^+$, there are three reversible diffusioncontrolled waves at -0.28, 0.58 and 0.86 V vs Fc^{+/0}, respectively. The first two waves are assigned to the successive oxidation of Ru^{II} to Ru^{III} and Ru^{III} to Ru^{IV}, as similar to the redox properties of $[(L^{N5-})Ru^{III-CI]^+$. The third wave of $[(L^{N5-})Ru^{III-OH]^+$ is caused by the oxidation of amide anion molety in L^{N5-}. DFT optimized structures of $[(L^{N5-})^{++}Ru^{IV}=O)]^{2+}$ displaying a strong radical character on the phenylamide bound to the Ru(IV) site (Figure 6c).

Different from the two electron oxidation wave $(Ru^{IV/II})$ of $[(tpy)(bpy)Ru-OH_2]^{2+75}$ at 0.36 V vs Fc^{+/0}, $[(L^{N5-})Ru^{III}-OH]^+$ displays successive oxidation and the first wave corresponding to $Ru^{III/II}$ is much lower than $[(tpy)(bpy)Ru-OH_2]^{2+,75}$ indicating that the electron-rich N₅⁻ ligand is helpful for lowering the oxidation potential. Moreover, the third ligand centered oxidation wave is conducive to achieving a formal $Ru^V=O$ valent form as $[(L^{N5-})^{++}Ru^{IV}=O]]^{2+}$, as similar to the complex I, $[(Por)^{++}Fe^{IV}=O]$, which is the key intermediate for P450 Enzyme.⁸⁴⁻⁸⁶ Interestingly, upon addition of water into the solution (Figure S12b), the first two waves of $[(L^{N5-})Ru^{III-}OH]^+$ are still reversible while a catalytic wave appears on the top of the wave of ligand-centered oxidation wave at 0.86 V vs Fc⁺⁰, indicating that $[(L^{N5-})^{++}Ru^{IV}=O)]^{2+}$ displays the potential to catalyze water oxidation.



Figure 2. CVs of 1 mM [(L^{N5-})Ru^{III}-CI]⁺, [(L^{N5-})Ru^{III}-OH]⁺ and [(tpy)(bpy)Ru-OH₂]²⁺ ⁷⁵ in propylene carbonate.

Electrocatalytic activity of $[(L^{N5-})Ru^{III}-OH]^+$ for water oxidation. The catalytic performance was investigated by electrochemical method in phosphate buffers (pH 7.0) at room temperature. Figure 3a shows the a cyclic voltammogram (CV) for $[(L^{N5-})Ru^{III}-OH]^+$ with a glassy-carbon working electrode (0.07 cm²) at scan rate of 100 mV/s. The CV displays three waves a 0.21, 0.81 and 1.1 V vs NHE, which is comparable to its redox properties in propylene carbonate. The difference is the third wave is irreversible and has significant current enhancement compared to the CV of the blank solution (black line). Figure 3b shows a current-normalized CV (i/ \sqrt{v} vs scan rate v) for [(L^{N5-})RuIII-OH]+ at scan rate from 50 to 900 mV/s. The normalized currents of the third wave were strongly depended on the scan rate consistent with a catalytic water oxidation process. Oxygen evolution was confirmed by bulk electrolysis at +1.20 V (vs Ag/AgCl) on an GC electrode (2 cm²) with 0.5 mM [(LN⁵⁻)Ru^{III}-OH]⁺ in 0.1 M PBS (pH 7.0). The formed oxygen was measured using a calibrated Ocean Optics FOXY probe (Figure 4a). For long-term electrolysis, 21 turnovers per catalyst were determined and the Faraday efficiency was approximately 80% during this catalytic process (Figure 4b). Notably, the onset potential of this catalytic water oxidation appears at ~ 1.0 V vs NHE which is approximately 700 mV lower than the classic single-site catalysts such as [(tpy)(bpy)Ru^{II}-OH₂]^{2+,75} and [(tpy)(bpz)Ru^{II}-OH₂]^{2+,74,77}



Figure 3. (a) CVs of 1.0 mM $[(L^{N5}-)Ru^{III}-OH]^+$ (red line) and blank (black line) at a glassy carbon (GC) electrode at 100 mV/s in 0.1 M pH 7.0 PBS; (b) Normalized CVs of 1.0 mM $[(L^{N5}-)Ru^{III}-OH]^+$ in 0.1 M pH 7.0 PBS at different scan rates.

RESEARCH ARTICLE



Figure 4. (a) Oxygen evolution during bulk electrolysis at the applied potential of 1.20 V vs Ag/AgCl. Conditions: 0.5 mM [(L^{N5-})Ru^{III}-OH]⁺; in 0.1 M pH 7.0 PBS; GC electrode (2 cm²). (b) Plot of current versus time during bulk electrolysis in 0.1 M pH 7.0 PBS at + 1.2 V (vs Ag/AgCl). Conditions: 0.5 mM [(L^{N5-})Ru^{III}-OH]⁺, working electrode: 2 cm² GC electrode.

Mechanistic analysis on water oxidation. To better understand the electrocatalytic mechanism of water oxidation, we further investigated the redox properties of $[(L^{N5-})Ru^{III}-OH]^+$ at different pH as well as kinetic analysis of the catalytic process.

(a) Pourbaix diagram of $[(L^{N5-})Ru^{III}-OH]^+$. As discussed above, the redox properties of $[(L^{N5-})Ru^{III}-OH]^+$ have been investigated by cyclic voltammetric (Figure S15 and Figure S19) and coulomb metric experiments. Figure 5 presents the Pourbaix diagram in details. The first reversible wave switched from pH-independent (Eq.1) to 56 mV/pH dependent (Eq.2) around pH 6.0, which is assigned to the following reactions,

$$[(L^{N5-})Ru^{II}-OH_2]^+ - e^- \rightarrow [(L^{N5-})Ru^{III}-OH_2]^{2+}$$
(Eq.1)
$$[(L^{N5-})Ru^{II}-OH_2]^+ - e^- - H^+ \rightarrow [(L^{N5-})Ru^{III}-OH]^+$$
(Eq.2)

In term of its redox potential, $[(L^{N5-})Ru^{II}-OH_2]^+$ is easily to be oxidized to $[(L^{N5-})Ru^{III}-OH]^+$ by O_2 in aqueous solution; this is well consistent with our observations as described in the above synthetic section. In addition, the p*K*a of $[(L^{N5-})Ru^{III}(OH_2)]^{2+}$ is approximately 6.0, which was extracted from the Pourbaix diagram.

The second quasi-reversible wave is strongly pH dependent with the slope of 130 mV/pH (4<pH<6, Eq.3) and 60 mV/pH (pH>6, Eq.4), which is correspond to the oxidative processes,

$[(L^{N5-})Ru^{III}-OH_2]^{2+} -e^{-}-2H^+ \rightarrow [(L^{N5-})Ru^{IV}=O]^+$	(Eq.3)
$[(I^{N5-})Ru^{III}-OH]^+ - e^ H^+ \rightarrow [(I^{N5-})Ru^{IV}=O]^+$	(Fa.4)

We note that, in contrast to $[(tpy)(bpz)Ru^{II}-OH_2]^{2+,74,77}$ the electrochemical conversion of $[(L^{N5-})Ru^{II}-OH_2]^{2+}$ to $[(L^{N5-})Ru^{IV}=O]^+$ is a successive one-electron redox process rather than a two-electron process which is observed in the case of $[(tpy)(bpz)Ru^{IV}=O]^{2+74,77}$ formation.

The generated [(L^{N5-})Ru^{IV}=O)]⁺ could be further oxidized via a ligand-centered one-electron process at 1.0 V vs NHE to give a formal [(L^{N5-})⁺⁺Ru^{IV}=O]²⁺ intermediate (Eq.5) and this process will be further discussed in details below. The formed [(L^{N5-})⁺⁺Ru^{IV}=O]²⁺ could react with H₂O to initiate the water oxidation process (Eq. 6) according to the O₂ evolution experiments discussed above.

 $[(L^{N5-})Ru^{IV}=O]^{+} - e^{-} \rightarrow [(L^{N5-})^{++}Ru^{IV}=O]^{2+}$ (Eq.5)

[(L^{N5-})⁺•Ru^{IV}=O]²⁺ + 2H₂O -2e⁻ →

$$[(L^{N5-})Ru^{III}-OH]^+ + 3H^+ + O_2$$
 (Eq. 6)



Figure 5. Pourbaix diagram of $[(L^{N5})Ru^{III}-OH]^+$ (1.0 mM, 298K) in 0.1 M PBS. Points indicate the pH values at which the electrochemistry study was performed; solid lines are the trend lines for each redox process. All data were determined by the differential potential voltammetry method using a glassy carbon electrode as the working electrode.

(b) Ligand-centered oxidation. The oxidation potential of $[(L^{N5-})^{+*}Ru^{IV}=O]^{2+}$ at 1.0 V vs NHE is much lower than the oxidation of $[(tpy)(bpy)Ru^{V}=O]^{2+75}$ and $[(tpy)(bpz)Ru^{V}=O]^{2+74,77}$ at ~1.7 V vs NHE. It is not realistic to ascribe this 700 mV shift to the electronic effect of L^{N5-} on the formation of $[(L^{N5-})^{+*}Ru^{IV}=O]^{2+}$. To further understand this process, DFT calculations were performed using PBE0⁹¹ functional and SMD implicit solvation model⁹² in Gaussian 09⁹³. For the potentials of three steps of oxidation of $[(L^{N5-})Ru^{III}-OH]^+$, calculations at the PBE0-GD3(BJ)/ma-def2-TZVP//PBE0-

(Eq. 8)

RESEARCH ARTICLE

GD3(BJ)/def2-SVP94-98 level gave 0.09 V, 0.75 V and 1.09 V, which fit the experimental values well. As spin analysis has been a powerful method in understanding the oxidation of metal complexes,⁹⁹⁻¹⁰⁰ Figure 6 shows the optimized structures and spin populations of [(L^{N5-})Ru^{III}-OH]⁺, [(L^{N5-})Ru^{IV}=O]⁺, and [(L^{N5-})⁺Ru^{IV}=O]²⁺, respectively. For the case of [(L^{N5-})Ru^{IV}=O]⁺, ligand oxidation process occurs from [(L^{N5-})Ru^{IV}=O]⁺ to [(L^{N5-})⁺·Ru^{IV}=O]²⁺, which can be revealed by spin population and spin density analysis. The sum of spin populations on the ligands of three species are 0.09, 0.03 and -0.72, respectively. This is consistent with the spin density of [(L^{N5-})+Ru^{IV}=O]²⁺ shown in Figure 6c. It clearly indicated that metal and ligand are antiferromagnetically coupled in [(L^{N5-})+Ru^{IV}=O]²⁺. In contrast, [(tpy)(bpy)Ru^{II}-OH₂]²⁺⁷⁵ and $[(tpy)(bpz)Ru^{II}-OH_2]^{2+74,77}$ do not show ligand oxidation when its Ru^V=O form is compared to its Ru^{IV}=O analogue. This process proves that L^{N5H} is a redox-active ligand critical for the observed low overpotential.

via Ru^{IV}=O mechanism to oxidize water at neutral pH with low overpotential.

(c) Kinetics analysis. Figure 7 shows that the current of both the diffusion-controlled waves and catalytic wave for water oxidation by [(L^{N5})⁺·Ru^{IV}=O]²⁺ are linearly dependent on the concentration of the catalyst, [(L^{N5-})Ru^{III}-OH]⁺. This suggests that the O-O bond formation should be achieved on a single-site in accordance with a water nucleophilic attack mechanism with [(L^{N5})+Ru^{IV}=O]²⁺ as the intermediate. Thus, the reversible wave at 0.2 V vs NHE for the Ru^{III/II} couple should obey the Randles-Svecik equation in Eq. 7 and the current of the catalytic wave could be expressed by Eq. 8.102

$i_d = 0.496 n_d FA$ [Cat .] $\sqrt{n_d F v D_{cat} / RT}$	(Eq. 7)
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0.4

E (V vs NHE)

0.8

1.2

$$i_{cat} = n_{cat} FA[Cat.] \sqrt{k_{obs} D_{cat}}$$

40

20 0

0

1



Figure 6. Spin densities analysis (at isovalue of 0.01) of different oxidation states of $[(L^{N5-})Ru^{II}-OH_2)]^+$, $[(tpy)(bpy)Ru^{II}-OH_2]^{2+75}$ and $[(tpy)(bpz)Ru^{II}-OH_2]^{2+,74}$, 77 respectively. Green and blue isovalue surfaces express α and β electrons respectively. Wave function analysis: Multiwfn.101

It is important to note that the O-O bond formation with Ru^{IV}=O, as oxidant, compared with Ru^V=O mechanism for [(tpy)(bpy)Ru^{II}- $OH_2)]^{2+75}$ and $[(tpy)(bpz)Ru^{II}-OH_2]^{2+,74,77}$ would have the advantage of a considerable decrease in overpotential. Meyer et al reported that [(tpy)(bpz)Ru^{IV}=O]²⁺⁷⁷ could react with H₂O in pH>11.6 phosphate buffer with the help of the basic form of the buffer, PO₄³⁻, at the second order rate constant about 5.4 M⁻¹ s⁻¹, however, [(tpy)(bpz)Ru^{IV}=O]²⁺ do not able to react with water around pH 7.0.77 This work reported here gives the first example

Figure 7. (a) CVs of different concentrations of I(L^{N5-})Ru^{III}-OHI⁺ in 0.1 M pH 7.0 PBS (b) linear regression of icat vs catalyst concentration, [Cat.].

2

[Cat.]/ mM

3

4

RESEARCH ARTICLE

where *F* is the Faraday constant, *A* is the electrode surface area, i_d is the peak current of the diffusion controlled wave, i_{cat} is the peak current of the catalytic wave, [Cat.] is the bulk concentration of the $[(L^{N5-})Ru^{III}-OH]^+$, D_{cat} is the diffusion coefficient of the catalyst, and $n_{cat} = 4$ is the electrochemical stoichiometry for water oxidation. According to the plot of i_{cat}/i_d versus $1/\sqrt{v}$ (Figure 8a), the observed rate constant for water oxidation catalysis, k_{obs} , was determined as 1.26 s⁻¹ at 1.0 V vs NHE pH 7.0 with $[HPO_4^{2-}] = 40$ mM. Figure 8b shows that the value of k_{obs} is dependent on $[HPO_4^{2-}]$ concentration from 0.05 – 0.20 mM by varying the phosphate buffer concentration with constant pH at 7.0, indicating that k_{obs} for water oxidation by $[(L^{N5-})^{+*}Ru^{IV}=O]^{2+}$ could be expressed as Eq. 9.

$$k_{obs} = k_{H_2O} + k_{Ru(IV)}^{HPO_4^{2-}} * [HPO_4^{2-}]$$
 (Eq. 9)

where $k_{Ru(IV)}^{HPO_4^{2-}} = 10.2 \text{ M}^{-1} \text{ s}^{-1}$ determined from the slope is the second order rate constant for the HPO₄²⁻ assisted WNA reaction (Eq. 10) and $k_{H_2O} = 0.90 \text{ s}^{-1}$ from the intercept corresponding to the intrinsic activity of [(L^{N5-})⁺⁺Ru^{IV}=O]²⁺ to react with water (Eq. 11).

$$[(L^{N5-})^{+}Ru^{IV}=O]^{2+} + HO-H^{---}OPO_{3}H^{2-} \rightarrow [(L^{N5-})Ru^{III}-OOH]^{+} + H_{2}PO_{4}^{-}$$
(Eq. 10)
$$[(L^{N5-})^{+}Ru^{IV}=O]^{2+} + H_{2}O \rightarrow$$

[(L^{N5-}) Ru^{III}-OOH]⁺ + H⁺(aq.) (Eq. 11)



Figure 8. (a) Plot of linear regression of $i_{cat'}i_d vs v^{-1/2}$. (b) Plots of $k_{obs} vs [HPO_4^{2-}]$ for $[(L^{N5-})^{+*}Ru^{IV}=O]^{2+}$ at pH 7, I = 0.46 at room temperature.

The rate constants for water oxidation by [(L^{N5-})+Ru^{IV}=O]²⁺ at pH 7.0, as well as by [(tpy)(bpz)Ru^{IV} =O]²⁺⁷⁷ at pH 7. 0 and 11.6, are summarized in Table 1. Interestingly, [(L^{N5-})+*Ru^{IV}=O]²⁺ displayed significant intrinsic activity on the reaction with water, however, [(tpy)(bpz)Ru^{IV}=O]²⁺⁷⁷ lacked reactivity toward water at pH 7.0. This indicates that the effect of ligand-center oxidation on water oxidation is higher than solely electronic tuning by an electron-deficient ligand, such as bpz used in [(tpy)(bpz)Ru^{IV}=O]^{2+.77} Additionally, k_{obs} for water oxidation is first order on [HPO42-], which is consistent with WNA reaction with HPO₄² as the proton acceptor base (Eq. 10). The second order rate constants, k_{HPO4}^{2-} at pH 7.0, is approximately 2 times faster than k_{PO4}^{2-} of the reaction of [(tpy)(bpz)Ru^{IV}=O]²⁺⁷⁷ although the basicity of HPO42- is ~5 pKa units lower than PO43-. It is further indicated that [(L^{N5-})+Ru^{IV}=O]²⁺ is a stronger electrophile, compared to [(tpy)(bpz)Ru^{IV}=O]^{2+,77} with the benefit of the ligandcentered oxidation.

(d) Catalytic cycle. The potential to generate $[(L^{N5-})^{+*}Ru^{IV}=O]^{2+}$ is closer to $[(tpy)(bpz)Ru^{IV}=O]^{2+}$,⁷⁷ indicating that $[(L^{N5-})^{+*}Ru^{IV}=O]^{2+}$ has the potential to react with H₂O to form the O-O bond. The solvent kinetic isotope effect (KIE= k_{H2O}/k_{D2O}) value of the catalytic process is approximately 1.4 determined by the CV measurement in D₂O (pD 7.48) and H₂O (pH 7.00), respectively (Figure S16). The catalytic current for water oxidation by $[(L^{N5-})^{+*}Ru^{IV}=O]^{2+}$ was also found to vary linearly with buffer concentrations with the controlled ionic strength of *I* =0.462 M in PBS (Figure S17 and S18). The appearance of the KIE and the term first order in $[HPO_4^{2^-}]$ for $[(L^{N5-})^{+*}Ru^{IV}=O]^{2+}$ is consistent with a water nucleophilic attack (WNA) water oxidation with HPO₄²⁻ as the proton acceptor base (Eq. 10).

To obtain more details of the overall catalytic process, DFT calculations were performed and the results are summarized in Figure 9. $[(L^{N5-})Ru^{III}-OH]^+$ is first oxidized to give $[(L^{N5-})Ru^{IV}=O]^+$ by proton coupled electron transfer. The following ligand-centered oxidation significantly improved the reactivity of the $[(L^{N5-})Ru^{IV}=O]^+$, and thus, the resulting $[(L^{N5-})^+Ru^{IV}=O]^{2+}$ could experience nucleophilic attack by water (WNA) to give an intermediate peroxide that could be further oxidized to release oxygen and close the cycle. For the WNA process, the presence of the HPO₄²⁻ could lower the reaction barrier and benefit the O-O bond formation. The calculated barrier is overestimated comparing with the kinetics observation because of the entropic contribution was significantly overestimated. ^[103-104] It is worth pointing that the oxidation of the ligand plays a crucial role in the initiation of the catalytic process with a Ru^{IV}=O at pH 7.0.

RESEARCH ARTICLE

Table 1. Summary of the rate constants for water oxidation by [(L^{N5-})**Ru^{IV}=O]²⁺ and [(tpy)(bpz)Ru^{IV}=O]²⁺⁷⁷



Figure 9. Free energy surface of water oxidation catalyzed by $[(L^{N5})Ru^{[I]}-OH]^+$. Structures of intermediates and transition states are shown with unimportant hydrogen hidden. The reference potential of 1.00 V is used to set up the thermodynamics. The thermodynamic favored buffer anion involved pathway is shown in solid line while the other is shown in dotted line.¹⁰³ Molecular structure visualization: CYLview.¹⁰⁴

Conclusion

In conclusion, regarding electrochemical catalytic water oxidation, a new family of mononuclear ruthenium complexes bearing oxidative electron-rich N⁵-ligand display impressive water oxidation performance with a lower overpotential (~ 183 mV) in 0.1 M phosphate buffer (pH 7.0). It is the first Ru-based molecular catalyst which could initiate water oxidation with an Ru(IV)=O intermediate in neutral aqueous solution. As inspired by the chemistry of [(Por)+Fe^{IV}=O] in P₄₅₀ enzyme, the oxidative ligand is involved in modulation of the electrophilic properties of the Ru(IV)=O. Such a conclusion is further supported by the DFT calculation. This work opens new avenue for the development of water oxidation catalysts that could drive the catalytic cycle with a

lower valent metal oxo intermediate. We note that the reactivity of Ru(IV)=O intermediates toward water oxidation could be significantly improved by the ligand oxidation, and we hope the insight reported here will lead to an extensive application of $(L)^+M^{n+}=O$ type intermediates in water oxidation catalysis and oxidative organic transformation.

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RESEARCH ARTICLE

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Keywords: artificial photosynthesis• water oxidation • redoxactive ligand • Ru(IV)=O intermediate

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

RESEARCH ARTICLE

Ru^{IV}=O not Ru^V=O: A new family of mononuclear ruthenium complexes bearing oxidative electron-rich ligand display impressive water oxidation performance with Ru^{IV}=O as key intermediate for O=O bond formation rather than Ru^V=O which is extensively proposed for water oxidation.



J. Shi, Y.-H. Guo, F. Xie, Q.-F. Chen, and M.-T. Zhang

Page No. – Page No.

Redox-Active Ligand Assisted Catalytic Water Oxidation by Ru(IV)=O Intermediate