Unexpected Ligand Lability in Condition of Water Oxidation Catalysis

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Abstract

In the search for rational design of improved water oxidation catalysts, enhanced catalytic activities were reported for single site Ru catalysis with Ru-iodide coordination. As these complexes are not initially capable of proton coupled electron transfer (PCET) and Ru=O formation, a proposal was put forward on the generation of catalytically active 7-coordinate Ru species. We tested this hypothesis by EPR and X-ray spectroscopy and found that $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ only serves as a precursor for formation of $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$. Upon oxidation with excess of Ce^{IV} the Ru-I bond quickly dissociates with formation of $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{3+}$ and $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ complexes. The catalytic steady state was composed of 95% $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ species. Thus, introducing the Ru-I bond into initial catalysts does not serve to improve catalyst design. This manuscript also shows how EXAFS can directly probe transition metal-halogen interaction for *in situ* catalysis.

Introduction

Ru based complexes are widely used in homogeneous catalysis [1, 2]. Some of them exist in a form which contains a Ru-halogen bond in the catalyst precursor or in the active form of the catalyst. When such complexes are dissolved in coordinating solvents or added to reaction mixtures, it is sometimes difficult to establish the dynamics of halogen exchange. For diamagnetic complexes, NMR can be used to monitor the resonance of organic ligands and draw conclusions about the halogen ligands' exchange with solvent [3] but this technique is not applicable for paramagnetic Ru^{III} , Ru^{IV} and Ru^{V} complexes and their intermediates. Here we show that X-ray absorption spectroscopy (XAS) can serve as a very sensitive and direct probe of the metal-halogen binding as well as report on the overall electronic structure of the Ru center.

This study focuses on analyzing the water oxidation mechanism in single site Ru based catalysts for artificial photosynthesis. The realization of artificial photosynthesis carries the promise of abundant and clean solar fuels. However, the process requires an efficient and durable water oxidation catalyst. Mononuclear Ru-based water oxidation catalysts are currently under active investigation in an effort to uncover the fundamental principles controlling their catalytic activity [3-13]. A mononuclear Ru-based catalyst usually contains polypyridine ligands and one water molecule coordinated to Ru. The role of ligands in catalytic water oxidation by mononuclear ruthenium complexes is summarized in a recent review by Zeng and coworkers [14]. Molecular Ru containing complexes remain the prime choice for mechanistic studies as series of complexes are available with varying redox potentials, ligand environment and catalytic activities. Thus, a detailed analysis of these complexes will help to understand overall principals controlling the catalytic water oxidation and result in design of more active molecules with higher stability.

In single site Ru catalysts, a water molecule bound to Ru^{II} is capable of proton coupled electron transfer (PCET) when both electron and proton are removed from the catalyst during oxidation to prevent charging of the complex. This process produces the oxidized $\text{Ru}^{\text{IV}}=\text{O}$ and $\text{Ru}^{\text{V}}=\text{O}$ species [8, 15-18]. However, some water oxidation catalysts have been reported which are seemingly incapable of PCET as they lack a ligand suitable for deprotonation, such as water [3, 19]. For instance, $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ catalyst lacks an H_2O bound to Ru but evolves more oxygen than the parent $[\text{Ru}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ complex [3]. This calls for an investigation of potential reasons for improved catalysis. The importance of steric strain on reactivity has been noticed for complexes with no water ligand on Ru [19]. To explain these unexpected observations the expansion of Ru coordination sphere to 7 has been proposed to accommodate water as a 7th ligand and allow for PCET and catalytic activity leading to O-O bond formation [3, 5]. Formation of 7-coordinated species was also implicated in water oxidation catalysis by $\text{Ru}^{\text{II}}(\text{X})_2\text{L}$ type complexes (where H_2L is 2,2'-bipyridine-6,6'-dicarboxylic acid and X can be monodentate ligand such as 4-picoline) [20, 21].

In this study we investigate claims of 7-coordinated Ru intermediate in $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ and the potential role of this new pathway for design of better catalysts of water oxidation. Our spectroscopic EXAFS (Extended X-ray Absorption Fine Structure) analysis has shown that in the catalytic cycle, a 7-coordinate Ru intermediate is not a major species. Instead, the $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ species was observed as catalytic steady state intermediate. Thus, inclusion of halogen atoms in the Ru coordination sphere instead of H_2O molecules will unlikely result in a new class of catalysts with significantly improved reactivity. Our results also illustrate significantly different behavior for Ru-I and Ru-Cl bonds under appropriate conditions for water oxidation. Ru-Cl interaction is retained under strongly oxidizing conditions over the investigated

period of time and the complex is not catalytically active. This observation reinforces the finding that $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ is a prerequisite of catalytic activity.

Experimental

Sample Preparation. Throughout this study the $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ (bpy = 2,2'-bipyridine, tpy = 2,2'; 6',2''-terpyridine) complex was used as a I^- salt. Note that all experiments with $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ salt dissolved in water should be performed immediately (within 2 minutes) to avoid any exchange of Ru-I with water. For optimal experimentation the $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ solution was aliquoted into small plastic tubes and frozen for further use. $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]\text{Cl}_2$ is obtained by incubation of $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]\text{Cl}$ in water for 24 h. Ultrapure (Type 1) water (resistivity 18.2 $\text{M}\Omega\text{ cm}$ at 25 °C, TOC 4 $\mu\text{g/L}$) was used for solutions. All samples were prepared in 0.1 M HNO_3 pH 1.0 (Catalog No. 225711 from Sigma Aldrich). Oxidant solutions were prepared fresh daily by dissolving $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$ in 0.1 M HNO_3 . A Cary 300 Bio UV-Vis spectrophotometer (Varian Inc.) was used to monitor UV-Visible spectra (5×10^{-5} M concentration). Solutions for preparation of electron paramagnetic resonance (EPR) samples were bubbled with argon to displaced dissolved oxygen.

EPR Measurements. Low-temperature X-band EPR spectra were recorded by using a Bruker EMX X-band spectrometer equipped with an X-Band CW microwave bridge. The sample temperature was maintained at 20 K, unless otherwise indicated, by use of an Air Products LTR liquid helium cryostat. Spectrometer conditions were as follows: microwave frequency, 9.65 GHz; field modulation amplitude, 10 G at 100 kHz; microwave power, 31.70 mW. Standard EPR sample tubes were filled with sample through all of the resonator space, a septum was placed on top and sample space was evacuated to prevent oxygen condensation. Whenever relative signal intensities are discussed, measurements were conducted on the same day and under the same

conditions to allow direct comparison of the signal intensities. Field calibration was checked versus a DPPH (2,2-diphenyl-1-picrylhydrazyl) standard.

Oxygen (O_2) Evolution Measurements. Oxygen evolution was measured with a PC-operated Clark type polarographic oxygen electrode from Oxygraph System (Hansatech Instruments Ltd.). The sample was housed within a hermetic borosilicate glass reaction vessel, thus preventing penetration of any atmospheric oxygen. Calibration was carried out by measurements of the signal from O_2 -saturated water in an open reaction vessel. Sodium dithionite, an oxygen depleting agent, was added to the water, and the drop in the signal was related to the solubility of oxygen in water at room temperature ($276.26 \mu\text{mol/L}$). The glass vessel was thoroughly washed with water and then 0.8 mL of 0.55 mM Ru solution in water was added. A defined number of Ce^{IV} equivalents (usually 20 equiv in 1 M HNO_3) were carefully added by means of a Hamilton syringe into the chamber through a plunger screw, and oxygen evolution was measured as a function of time. The dilution of Ce^{IV} solution was adjusted to 10:1 to allow for final $\text{pH} = 1$.

Ru K-edge X-ray Absorption Spectroscopy (XAS) Measurements. Ru K-edge XAS spectra were collected at the Advanced Photon Source (APS) at Argonne National Laboratory on the BM-20 beamline at incident photon energy 23 keV and average current of 100 mA. The radiation was monochromatized by a Si(110) crystal monochromator. The intensity of the X-rays was monitored by three ion chambers (I_0 , I_1 and I_2) filled with 70% nitrogen and 30% argon and placed before the sample (I_0) and after the sample (I_1 and I_2). Ru metal was placed between the I_1 and I_2 and its absorption was recorded with each scan for energy calibration. Plastic (Lexan) EXAFS sample holders (inner dimensions of 12 mm x 3 mm x 3 mm) filled with frozen solutions were inserted into pre-cooled (20 K) cryostat. The samples were kept at 20 K in a He atmosphere at ambient pressure. Data were recorded as fluorescence excitation spectra using a

Ge 13-element energy-resolving detector. Solid samples were diluted with BN powder in a 1:5 ratio, pressed between mylar tape, and measured in the cryostat in transmission mode. In order to reduce the risk of sample damage by X-ray radiation, 80% flux was used in the defocused mode (beam size 1×8 mm) and no damage was observed in multiple scans. The samples were also protected from the X-ray beam during motor movements by a shutter synchronized with the scan program. Additionally, low flux measurements (only 10% of beamline flux) were done on reactive intermediates to demonstrate the same EXAFS results. No more than 5 scans were taken at each sample position at any condition.

Ru XAS energy was calibrated by the first maxima in the derivative of the ruthenium metal XANES (X-ray Absorption Near Edge Structure) spectrum (22117 eV). EXAFS scan with 10 eV steps in the pre-edge region (21967-22102 eV), 1-eV steps (22102-22117 eV) through the edge and 0.05 $\text{\AA}^{-1}$ steps from $k = 2.0$ -16 $\text{\AA}^{-1}$ were used. As reference compounds for high Ru oxidation states, Ru^{IV} and Ru^{V} , Ru^{IV} oxide and tetra-n-propylammonium bis-2-hydroxy-2-ethylbutyrato(oxo) ruthenate(V)[22] were used.

Extended X-Ray Absorption Fine Structure (EXAFS) Data Analysis. The Athena software was used for data processing[23]. The energy scale for each scan was normalized using a ruthenium metal standard, and scans for same samples were added. Data in energy space were pre-edge corrected, normalized, deglitched (if necessary), and background-corrected. The processed data were next converted to the photoelectron wave vector (k) space and weighted by k^3 . The electron wave number is defined as $k = [2m(E - E_0)/\hbar^2]^{1/2}$, where E_0 is the energy origin or the threshold energy. The k -space data were truncated near the zero crossings ($k = 3.90$ to $15.20 \text{ \AA}^{-1}$) before Fourier transformation. The k -space data were transferred into the Artemis Software for curve fitting. To fit the data, the Fourier peaks were isolated separately, the peaks were grouped

together, or the entire (unfiltered) spectrum was used. The individual Fourier peaks were isolated by applying a Hanning window to the first and last 15% of the chosen range, leaving the middle 70% untouched. Curve fitting was performed using ab initio-calculated phases and amplitudes from the FEFF8 program from the University of Washington [24]. Ab initio-calculated phases and amplitudes were used in the EXAFS equation [25]

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{eff_j}(\pi, k, R_j) e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda_j(k)} \sin(2kR_j + \phi_{ij}(k)) \quad (S1)$$

where N_j is the number of atoms in the j th shell, R_j is the mean distance between the absorbing atom and the atoms in the j th shell, $f_{eff_j}(\pi, k, R_j)$ is the ab initio amplitude function for shell j , and the Debye–Waller term $e^{-2\sigma_j^2 k^2}$ accounts for damping caused by static and thermal disorder in absorber–backscatterer distances. The mean free path term $e^{-2R_j/\lambda_j(k)}$ reflects losses caused by inelastic scattering, where $\lambda_j(k)$ is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term $\sin(2kR_j + \phi_{ij}(k))$, where $\phi_{ij}(k)$ is the ab initio phase function for shell j . This sinusoidal term shows the direct relation between the frequency of the EXAFS oscillations in k -space and the absorber–backscatterer distance. S_0^2 is an amplitude reduction factor.

The EXAFS equation (Eq. S1) was used to fit the experimental Fourier isolated data (q -space) as well as unfiltered data (k -space) and Fourier transformed data (R -space) using N , S_0^2 , E_0 , R , and σ^2 as variable parameters (see fit results in Table 1). N refers to the number of coordination atoms surrounding Ru for each shell. The quality of fit was evaluated by R -factor and the reduced χ^2 value. The deviation in E_0 should be less than or equal to 10 eV. R -factor less than 2% denotes that the fit is good enough, whereas R -factor between 2% and 5% denotes that the fit is correct

within a consistently broad model.⁵ The reduced χ^2 value is used to compare fits as more absorber–backscatter shells are included to fit the data. A smaller reduced χ^2 value implies a better fit. Similar results were obtained from fits done in k -, q -, and R -spaces.

Cl K-edge XANES measurements. Cl K-edge XANES spectra were collected at the Advanced Photon Source (APS) at Argonne National Laboratory on beamline 9-BM at a photon energy of 2.3–3.0 keV and an average current of 100 mA. A Si(111) crystal monochromator with approximately 0.3 eV energy resolution was used, and the intensity of the incident X-rays were monitored by an ion chamber (I_0) in front of the sample. The solution samples were prepared by dissolving the [Ru(bpy)(tpy)Cl]Cl at 1 mM concentration in 0.1 mM HNO₃ (pH=1) or in water. Data on solutions were recorded as fluorescence excitation spectra using a 4-element energy-resolving detector. The solution samples were kept at 80 K using a Linkam cryostage in a He atmosphere at ambient pressure. To reduce X-ray induced sample damage, 80 % flux was used; no damage was observed in consecutive scans. No more than three scans were taken at each sample position. A Ru metal standard was measured every day for energy calibration, with the edge position being determined by the inflection point evaluated as second derivative zero-crossing.

Results and Discussion

Here we report EPR and X-ray spectroscopy analysis of $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ complex to characterize reactive intermediates under water oxidation conditions using cerium ammonium nitrate (Ce^{IV}) as chemical oxidant in 0.1 M HNO_3 . All solutions of $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ were used immediately to avoid exchange of Ru-I with water. The spectroscopic behavior of $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]^+$ is found to be critically different from the one reported for the similar $[\text{Ru}(\text{bpy})(\text{tpy})\text{Cl}]^+$ complex [8]. Figure 1 shows EPR spectra obtained after oxidation of $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ with 1 to 7 equivalents of Ce^{IV} . While oxidation of $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]^+$ and $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ with one equiv of Ce^{IV} results in full conversion to corresponding Ru^{III} complexes with distinct EPR signals [8], addition of 1 equiv of Ce^{IV} to $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ results in an EPR silent sample. The addition of 2 to 7 equiv to solutions of $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ results in an EPR signal with a g-tensor identical to $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{3+}$, with a maximal intensity detected with 5 equiv of Ce^{IV} (Figure 1 and Table S1). We have not observed any spectral EPR components which can be assigned to the $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{I}]^{2+}$ complex or iodide-containing radicals in samples frozen within 30 sec after addition of Ce^{IV} (data not shown) as well as in samples incubated with Ce^{IV} for 2 minutes (Figure 1). Thus, the $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{I}]^{2+}$ complex is likely unstable. The larger number of oxidative equivalents required to produce $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{3+}$ is likely due to oxidation of iodide ions. Further oxidation of $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{3+}$ to $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ explains the decrease in $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{3+}$ EPR signal after increasing Ce^{IV} concentration. In the $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ complex at pH=1, the oxidation potential of $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}} \sim 1.05\text{V}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}} \sim 1.24\text{V}$ are relatively close. According to the Pourbaix diagram [26], conversion of I_2 to IO_3^- happens around 1.15-1.2 V, which is very similar to the potential for $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ conversion. This explains why with 7 equiv of Ce^{IV}

$[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{3+}$ remains present in the mixture as oxidative Ce^{IV} equivalents are used for oxidation of I^- ligand and counter ion. The addition of 20 equiv of Ce^{IV} results in an EPR silent sample with a residual EPR signal that is very similar to the one recorded for $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ oxidized with 20 equiv, (Figure S1, S2 and S3).

Figure 1. X-Band EPR (20 K) of $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ complex oxidized with 1-7 equiv of Ce^{IV} and frozen after mixing 2 min, compared with $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{3+}$ (black dashed) obtained by oxidation of $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ with 1 equiv of Ce^{IV} . Catalyst concentration is 1 mM in 0.1 M HNO_3 .

To verify changes in the Ru oxidation state and Ru-I bonding under oxidation we used Ru K-edge X-ray absorption spectroscopy (XAS), a technique which is uniquely sensitive to the oxidation state and coordination environment of Ru centers [8, 16, 27]. Figure 2A shows Ru K-edge XANES spectra for $[\text{Ru}(\text{bpy})(\text{tpy})\text{I}]\text{I}$ for samples frozen within 30 seconds following the addition of Ce^{IV} . Measurements were done at 20K and with a defocused X-ray beam to avoid radiation damage. The spectra show a small shift indicating only partial oxidation of the Ru^{II}

center upon adding 1 and 2 equiv of Ce^{IV} (Figure 2A). Paired with the results of EPR, this suggests that oxidation of another component in the system (*e.g.*, iodide) takes place. In $[\text{Ru}(\text{bpy})(\text{tpy})\text{Cl}]^+$ and $[\text{Ru}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$, the addition of 1 equiv of Ce^{IV} results in the formation of an Ru^{III} complex as verified by XANES and EPR [8].

Figure 2. Normalized Ru K-edge XANES (A) and Fourier transforms of k^3 -weighted Ru EXAFS (B) of the starting $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ (black), $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ complex oxidized with 1 equiv (purple), 2 equiv (light blue), and 20 equiv (black dashed line) of Ce^{IV} . There is 1 mM catalyst concentration in 0.1 M HNO_3 . Samples were frozen 30 sec after mixing and measured at 20 K.

Figure 3. Normalized Ru K-edge XANES (A) and Fourier transforms of k^3 -weighted Ru EXAFS (B) of the starting $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ (black) and $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ (red) complexes; $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ complex oxidized with 20 equiv (black dashed line) of Ce^{IV} and $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ oxidized with 20 equiv of Ce^{IV} (red dashed line). There is 1 mM catalyst concentration in 0.1 M HNO_3 .

Ru K-edge EXAFS was used to verify changes in the Ru-I interaction during oxidation (Figure 2B). Ru-I absorber-backscatter pair gives an intense peak at an apparent distance of 2.4 Å. The

intensity of this peak decreases with addition of 1 and 2 equiv of Ce^{IV} and fully disappears after adding 20 equiv. Thus, addition of even 1 and 2 equiv of Ce^{IV} already decreases the number of complexes with a Ru-I bond. Under catalytic conditions, the Ru-I interaction disappears within 30 sec of sample mixing. EXAFS results firmly rule out the presence of a Ru-I bond under catalytic conditions and thus the formation of 7-coordinated intermediate $[\text{Ru}^{\text{x}}(\text{bpy})(\text{tpy})(\text{H}_2\text{O})\text{I}]^{\text{x}-1}$ as a catalytically relevant species. The behavior of $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]$ is critically different from the analogous $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]$ complex. While both complexes engage in halogen exchange with solvent when the Ru center is in the oxidation state 2+ with 50% conversion at 3 h (Ru-Cl) and 4.3 h (Ru-I) as determined by NMR studies [3], stabilization of the Ru-Cl bond was observed upon oxidation of the catalyst with Ce^{IV} [8]. Cl exchange in the $\text{Ru}^{\text{II}}\text{-Cl}$ complexes is well documented in the literature [28-30], while fewer studies are available for Ru^{III} complexes. One would expect that Ru^{III} with increased positive charge will bind negatively charged halogen ligand much stronger. To verify this we directly monitored the Ru-Cl bond under various reaction conditions by Cl K-edge XANES (Figure 4). We have used the effect described earlier for complexes with Mn-Cl [31] and V-Br [32] bonds, namely the appearance of the pre-edge in the Cl absorption K-edge upon binding to the transition metal. Figure 4(A) shows Cl K-edge XANES for $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]\text{Cl}$ incubated in water for 2 min, 30 min and 4 hours and frozen for XANES analysis. The spectra show two pre-edge peaks at 2821.8 and 2822.8 eV. Their intensities decreases significantly after incubation for 4 hours which is in good agreement with earlier NMR studies [3]. Figure 4B shows Cl K-edge spectra of $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}$ generated by oxidation with 1

Figure 4. (A) Cl K-edge of $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]^+$ dissolved in water and frozen after 2 min, 30 min and 4 hours. Water solution of NaCl is displayed for comparison to show spectrum of free Cl^- ion. (B) Cl K-edge of $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}$ prepared by oxidation of $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]^+$ with 1 eq of Ce^{IV} and frozen 2 min, 30 min and 4 hours after preparation. (C) Cl K-edge of $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]^+$ oxidized with 20 eq of Ce^{IV} and frozen 2 min, 30 min and 4 hours after preparation. 1mM catalyst concentration in 0.1 M HNO_3

equiv of Ce^{IV} . Interestingly, $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}$ shows more intense and further separated pre-edge peaks with maximums at 2819.7 and 2822.1 eV. This is likely due to an increase in the Ru-Cl orbital mixing due to shortening of the Ru-Cl bond in the $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}$ complex. When freshly dissolved (less than 2 minutes) $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]\text{Cl}$ is oxidized with 1 equiv of

Ce^{IV} to generate [Ru^{III}(bpy)(tpy)Cl]²⁺ and the latter is left in solution for an extended period of time (up to 4 hours) no decrease in pre-edge intensity with time was noted (Figure 4B). To check stability of the Ru-Cl bond under catalytic conditions, we measured catalytic mixtures prepared with 20 equiv of Ce^{IV}, Figure 4C. We found that the amount of oxidant (up to 20 equiv) does not affect exchangeability of Ru^{III}-Cl and does not cause Ru-Cl bond dissociation.

The behavior of [Ru^{III}(bpy)(tpy)I]²⁺ is critically different and cannot be predicted based on the behavior of the [Ru^{III}(bpy)(tpy)Cl]²⁺ complex or available literature. The instability of [Ru^{III}(bpy)(tpy)I]²⁺ can be rationalized by the following proposed reaction sequence which implies homolytic dissociation of Ru-I occurring much faster than ligand exchange:

From this scheme it follows that the [Ru(bpy)(tpy)I]I complex converts into [Ru^{II}(bpy)(tpy)H₂O]²⁺ upon oxidation and final product of I[•] oxidation is likely IO₃⁻ according to its Pourbaix diagram [26]. To verify this, Figure 3 compares XANES and EXAFS spectra of the starting [Ru(bpy)(tpy)H₂O]²⁺ and [Ru(bpy)(tpy)I]I catalysts and catalytic species in these two systems achieved upon oxidation with 20 equiv of Ce^{IV}. While XANES and EXAFS of the starting materials are very different, spectra of their reaction mixtures are virtually identical. The inflection points of 20 equiv Ce^{IV} [Ru(bpy)(tpy)H₂O]²⁺ and [Ru(bpy)(tpy)I]I spectra are the same indicating the oxidation state of the iodine complex is Ru^{IV}. The Ru^{IV} oxidation state was earlier verified for [Ru(bpy)(tpy)H₂O]²⁺ using XANES with reference

Table 1. Parameters of EXAFS fits

Fit	Shell, N ^a	R, Å	σ ² (10 ⁻³)	R-factor	Reduced χ-square
[Ru ^{II} (bpy)(tpy)I] ^{I+}					
1	Ru-N, 6	2.04	5.7	0.874	44403
2	Ru-N, 5	2.07	4.6	0.032	2060
	Ru-I, 1	2.73	1.2		
3	Ru-N, 5	2.08	4.7	0.004	327
	Ru-I, 1	2.74	1.2		
	Ru-C, 10	3.13	14.4		
[Ru ^{II} (bpy)(tpy)I] ^{I+} + 1 equiv Ce ^{IV}					
4	Ru-N, 5	2.09	3.6	0.011	284
	Ru-I, 1	2.75	2.0		
	Ru-C, 10	3.15	15.8		
[Ru ^{II} (bpy)(tpy)I] ^{I+} + 2 equiv Ce ^{IV}					
5	Ru-N, 5	2.05	3.2	0.040	365
	Ru-I, 1	2.74	3.5		
	Ru-C, 10	2.92	3.5		

6	Ru-N, 5	2.05	3.6	0.040	365
	Ru-I, 0.5	2.73	1.1		
	Ru-C, 10	2.94	5.0		
[Ru ^{II} (bpy)(tpy)I] ¹⁺ + 20 equiv Ce ^{IV} , peak I					
7	Ru-N, 6	2.07	5.7	0.074	2286
8	Ru-O, 1	1.78 ^b	4.4	0.001	543
	Ru-N, 5	2.09	5.2		
[Ru ^{II} (bpy)(tpy)I] ¹⁺ + 20 equiv Ce ^{IV}					
9	Ru-N, 6	2.07	6.0	0.419	1636
10	Ru-N, 6	2.04	5.2	0.123	623
	Ru-C, 10	2.91	7.6		
11	Ru-O, 1	1.77 ^b	3.1	0.047	568
	Ru-N, 5	2.09	5.6		
	Ru-I, 0.1	2.69	0.03		
	Ru-C, 10	3.6	13.9		
12	Ru-N, 6	2.06	5.6	0.101	719
	Ru-I, 0.1	2.67	0.7		

	Ru-C, 10	2.97	11.4		
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^a N - Number of vectors is given per Ru center; $S_0^2 = 1$ was fixed. [b] $Ru^{IV}=O$ from DFT 1.81 Å.

compounds and EPR [8]. Both $[Ru(bpy)(tpy)H_2O]^{2+}$ and $[Ru(bpy)(tpy)I]I$ catalyst achieve close to 95% conversion to the Ru^{IV} oxidation state (Figure 3A). Table 1 compares EXAFS fits for the complexes under catalytic $[Ru(bpy)(tpy)I]I$ complexes [3]. This is in good agreement with spectroscopic results which show virtually indistinguishable structures of Ru species under catalytic conditions. However, $[Ru(bpy)(tpy)I]I$ eventually evolved about twice as much oxygen as shown by their turnover numbers (TON) [3]. The previous O_2 evolution results were reported for PF_6^- salts and catalysts were introduced into reaction mixture in acetonitrile [3]. We remeasured O_2 evolution using the same compounds and same conditions as in spectroscopic experiments with a Clark electrode immersed in the reaction mixture (Figure S4). Figure S4 shows that $[Ru(bpy)(tpy)I]I$ is less active than $[Ru(bpy)(tpy)H_2O]^{2+}$ under the condition of relatively low (20 equiv) Ce^{IV} concentration. This is not surprising and is in agreement with the trend observed by EPR. Some Ce^{IV} equivalents are used oxidizing an iodide ligand which effectively lowers the Ce^{IV} concentration and results in less efficient catalysis. This effect is less apparent under large (5000 equiv) excess of Ce^{IV} used for determination of TON. Under such condition, the initial rates of O_2 evolution are the same for both complexes [3] showing a minimal effect of I^- ligand on the overall mechanism. The presence of 5% CF_3CH_2OH in the reaction mixture results in the delayed (by about 50 s) O_2 evolution for $[Ru(bpy)(tpy)H_2O]^{2+}$ complex (Figure S4). $[Ru(bpy)(tpy)I]I$ is not soluble in water and thus was studied only in 5% CF_3CH_2OH .

Conclusions

[Ru(bpy)(tpy)I]I water oxidizing catalyst displays ligand lability, quickly loses the ruthenium-iodine bond upon oxidation and generates $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ reactive species. This behavior contrasts the properties of [Ru(bpy)(tpy)Cl]Cl which retains Ru-Cl bond and does not serve as a water oxidation catalyst. Thus, the formation of the $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ is a prerequisite for water oxidation catalysis. A detailed mechanism of its reaction with water (directly or via other intermediates) is currently unknown. X-ray spectroscopy is broadly applicable to a wide range of transition metal catalysts where catalyst precursor or catalytically relevant species having a transition metal-halogen bond. XANES at the Cl K-edge allows quick measurement and reports on both the presence of a metal-Cl bond and electronic structure (oxidation state) of the metal center under catalytic conditions.

Notes and references

Supporting information: EPR spectra, O₂ evolution results.

The authors declare no competing financial interests.

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Graphical Abstract

$[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ was reported to have enhanced catalytic activity in water oxidation.

EPR and X-ray absorption spectroscopy were used to study catalytic mechanism.

We determined that Ru-iodide bond is not sustained under catalytic conditions.

$[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{I}]^+$ serves as a precursor to a $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ catalytic intermediate.

$[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{Cl}]^+$ sustains Ru-Cl bond and is not a catalysts for water oxidation.