



Article

Subscriber access provided by Queen Mary, University of London

Evidence for Oxidative Decay of a Ru-Bound Ligand During Catalyzed Water Oxidation

Husain Noman Kagalwala, Lianpeng Tong, Ruifa Zong, Lars Kohler, Mårten S.G. Ahlquist, Ting Fan, Kevin J Gagnon, and Randolph P. Thummel

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.6b03278 • Publication Date (Web): 06 Mar 2017 Downloaded from http://pubs.acs.org on March 6, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Evidence for Oxidative Decay of a Ru-Bound Ligand During Catalyzed Water Oxidation

Husain Kagalwala,^{a‡} Lianpeng Tong,^{a‡} Ruifa Zong,^a Lars Kohler,^a Mårten S. G. Ahlquist,^b Ting Fan,^b Kevin J. Gagnon^c and Randolph P. Thummel^a*

^aDepartment of Chemistry, 112 Fleming Building, University of Houston,

Houston, TX 77204-5003, ^bDivision of Theoretical Chemistry & Biology, School of

Biotechnology, KTH Royal Institute of Technology, 10691 Stockholm, Sweden,

^cAdvanced Light Source, Lawrence Berkeley National Lab,

1 Cyclotron Rd., Berkeley, CA 94720

ABSTRACT

In the evaluation of systems designed for catalytic water oxidation, ceric ammonium nitrate (CAN) is often used as a sacrificial electron acceptor. One of the sources of failure for such systems is oxidative decay of the catalyst in the presence of the strong oxidant CAN ($E_{ox} = +1.71$ V). Little progress has been made in understanding the circumstances behind this decay. In this study we show that a 2-(2'-hydroxphenyl) derivative (LH) of 1,10-phenanthroline (phen) in the complex [Ru(L)(tpy)]⁺ (tpy = 2,2';6',2"-terpyridine) can be oxidized by CAN to a 2-carboxyphen while still bound to the metal. This complex is, in fact, a very active water oxidation catalyst. The incorporation of a methyl substituent on the phenol ring of LH slows down the oxidative decay and consequently slows down the catalytic oxidation. An analogous system based on bpy (2,2'-bipyridine) instead of phen shows much lower activity under the same conditions. Water molecule association to the Ru center of [Ru(L)(tpy)]⁺ and carboxylate donor dissociation was proposed to occur at the trivalent state. The resulting [Ru^{III}–OH₂] was further oxidized to [Ru^{IV}=O] via PCET process.

KEYWORDS: Mononuclear Ru catalysts, water oxidation, anionic ligands, 2carboxyphenanthroline, ligand decay

INTRODUCTION

 During the past several decades the objective of using solar energy to convert water into its elements has inspired a tremendous amount of work devoted to the design of effective photocatalysts to drive this process.¹⁻² Special focus has been on water oxidation, which is considered to be a bottleneck in achieving total water splitting.³ An important class of compounds that is being developed for this purpose involves transition metal complexes of polypyridine-type ligands.⁴⁻⁵ Some of the earliest reported catalysts were mononuclear Ru(II) complexes involving 2,2'-bipyridine (bpy), 2,2'; 6,2"-terpyridine (tpy), 1,10-phenanthroline (phen), and 2,9-di(pyrid-2'-yl)-1,10-phenanthroline (dpp).⁶⁻¹⁰

There are two fundamental features that are desirable in an effective water oxidation catalyst (WOC). Firstly, the catalyst should exhibit a high turnover frequency (TOF) meaning that it should facilitate water decomposition at a fast rate. Secondly, the catalyst should be very stable under the reaction conditions. Ideally, the catalyst will provide many millions of turnovers before becoming inactive. For a metal-polypyridine catalyst a likely decomposition pathway would involve oxidation of the polypyridine ligand, leading to fragmentation of the complex and ultimately release of the metal.¹¹⁻¹² Sometimes the metal or metal oxide is generated as a nanoparticulate material and these metal nanoparticles have been shown to serve as somewhat sluggish but quite effective WOCs.¹³⁻¹⁴

In terms of catalyst design, it seemed important to have a water molecule bound to the metal center.^{7, 15-16} This was further established by studies carried out using $[Ru(tpy)(bpy)X]^+$ type complexes.¹⁷⁻¹⁸ However, it was also discovered that water could add to coordinatively saturated Ru when the metal is first converted to a higher oxidation state.¹⁹ The consequential involvement of a Ru species with seven ligands demanded geometric features that allowed the formation of the required pentagonal bipyramid geometry. It was found that the two fused 5-membered chelate rings of a Ru-bound tpy would not allow the formation of a pentagonal bipyramid and thus $[Ru(tpy)_2]^{2+}$ was not an active catalyst for water oxidation. However, by expanding the size of one of the chelate rings to 6 atoms, a complex such as **1**(Scheme 1), after losing two electrons, would allow the attack of water and the consequent 7-coordinate geometry.²⁰

Electronic effects have also been shown to play a key role in the design of effective water oxidation catalysts. In particular, anionic ligands are expected to stabilize higher oxidation states

of the metal and thus lower the overall energy demands of catalyzed water oxidation.²¹⁻²² This concept has been elegantly demonstrated by Sun and coworkers who examined Ru complexes of 6,6'-dicarboxybpy and 2,9-dicarboxyphen.²³ Both systems were effective water oxidation catalysts. Herein we present our findings on a family of $[Ru(tpy)(N^N^O)]^+$ complexes (Scheme 1) used as water oxidation catalysts, with CAN as the sacrificial electron acceptor. We incorporated both the steric advantage of 6,5-chelation as well as the stabilizing effect of an anionic ligand by examining the 2-phenoxyphen system **2a** and comparing it against its 5,5-chelated 2-carboxyphen analog, **4** (Scheme 1). Expecting to see a difference in O₂ evolution activity, we instead obtained strong evidence for the oxidative decay of the 2-phenoxyphen ligand and its subsequent conversion into 2-carboxyphen while still bound to the metal. Using the methyl derivative **2b** slows down the rate of this conversion. Complex **4** was thus revealed to be the authentic catalyst as supported by ¹H-NMR, ESI-MS, X-ray and theoretical analysis. The related bpy-based complexes **3a,b** and **5** showed much lower activity, highlighting the importance of designing stable catalysts as well as moving towards more benign oxidizing agents.



Scheme 1. Complex 1, and family of [Ru(tpy)(N^N^O)]⁺ complexes 2-5 studied in this work

RESULTS AND DISCUSSION

Preparation and Characterization of the Catalysts

The phenanthrolinyl phenol ligand **10a** was prepared in three steps. First *o*-bromoanisole (**6a**) was converted to the corresponding boronic acid **7a** which was then coupled with 2-chloro-1,10-phenanthroline (**8**) to provide the methoxyphen derivative **9a**. Cleavage of the ether with HBr gave the phenol **10a** which then was used to prepare the heteroleptic complex **2a**. The analogous

methyl substituted ligand **10b** and its Ru^{II} complex **2b** were prepared in a similar fashion. A parallel route was followed for the preparation of the analogous phenol substituted bpy ligands**13a** and **13b**. These ligands, in turn, provided the heteroleptic complexes **3a** and **3b**. The synthesis of complex **5** was reported in an earlier work²⁴ and the complex **4** resulted from the treatment of [Ru(tpy)Cl₃] with 2-carboxy-1,10-phenanthroline (**14**). All these synthetic routes are outlined in Scheme 2. The ligands, complexes and intermediates all gave clear ¹H NMR spectra that allowed their unambiguous structure assignment (see Figure S1 and S2 for ¹H NMR of all phen and bpy-based complexes, respectively).



Scheme 2. Synthesis of complexes 2-5.

The electronic absorption spectra of the complexes **2-5** were measured in acetonitrile and the data is recorded in Table 1 as well as Figure S3. The phenoxy complexes **2a,b** and **3a,b** show a metal-to-ligand charge transfer (MLCT) absorption in the 525-529 nm range as well as a very weak low energy absorption at 714-718 nm. The carboxyphen and carboxybpy complexes **4** and **5** show a somewhat stronger MLCT absorption at 488-491 nm.

 The electrochemical properties of the complexes were measured by cyclic voltammetry and the redox potentials are recorded in Table 1. All four phenoxy complexes show very similar and reversible first oxidation potentials in the range of +0.42-0.46 V. This potential is substantially below the potential of +1.28 V recorded for $[Ru(tpy)_2]^{2+,20}$ meaning that the electron-donating phenoxy substituent helps to stabilize Ru^{III} allowing Ru^{II/III} oxidation to proceed much more readily. The reductions of **2a,b** and **3a,b** involve an electron being added to the most electronegative ligand which is tpy. The first reduction occurs at -1.45 to -1.47 V and the second reduction is observed at -1.79 to -1.80 V, somewhat more negative than the parent $[Ru(tpy)_2]^{2+}$.

Table 1. Electronic absorption^a and electrochemical properties^b of Ru complexes.

Complex	$\lambda_{\rm max} / {\rm nm} \left(\epsilon / {\rm M}^{-1} {\rm cm}^{-1}\right)$	$E_{1/2}^{\text{ox}}(\Delta E)$	$E_{1/2}^{red} (\Delta E)$
[Ru(tpy) ₂] ²⁺	270(43650), 308(70794), 475(16596)	1.28	-1.27 (ref 15)
2a	235 (55100), 273 (48100), 294 (35300, sh), 313 (31700), 320 (29300, sh), 376 (18300), 470 (7970, sh), 525 (10000), 716 (1580)	0.45 (66), 1.00 ^d , 1.55 ^d , 1.79 ^d	-1.47 (70), -1.79 (71)
2b	234 (45600), 274 (42900), 292 (32200, sh), 312 (28600), 322 (25800, sh), 382 (14400), 469 (7290, sh), 525 (9020), 718 (1370)	0.42 (66), 1.05 ^d , 1.35 ^d , 1.70 ^d	-1.46 (70), -1.79 (70)
3a	237 (44000), 273 (33900), 315sh (30800), 324 (33500), 348sh (15800), 527 (8740), 715 (1820)	0.46 (57), 1.03 ^d , 1.24 ^d , 1.60 ^d	-1.45 (63), -1.79 (70)
3b	238 (43700), 272 (36700), 313 (30700), 324 (30000), 342sh (16800), 529 (8710), 714 (1390)	0.46 (60), 1.05 ^d , 1.27 ^d , 1.47 ^d	-1.45 (71), -1.80 (73)

4	230 (51800), 272 (67900), 313 (40100), 357 (4820), 416 (6280, sh), 488 (15700)	0.86 (97), 1.10 ^d	-1.36 (71) ^c , - 1.63 (63) ^c
5	233 (29200), 244sh (25900), 274 (31300), 296 (40200), 314 (36300), 364 (6880), 491 (12600)	0.87 (61), 1.05 ^d	-1.37 (67), -1.64 (73)

^aMeasured using CH₃CN solutions (10 μ M). ^bRecorded in CH₃CN under Ar atmosphere, using 1 mM analyte and 0.1 M N(Bu)₄PF₆ as supporting electrolyte; E_{1/2} = (E_{pa} + E_{pc})/2 in volts versus SCE, $\Delta E = (E_{pa} - E_{pc})$ in mV. ^cQuasi-reversible. ^dIrreversible, depicts E_{pa} values only.

The carboxy complexes **4** and **5** are also self- consistent with $Ru^{II,III}$ oxidation occurring at +0.86-0.87 V and reductions at -1.36 to -1.37 V and -1.63 to -1.64 V. It is interesting to note that even though their redox properties are almost identical, **4** and **5** show very different WOC activity, as demonstrated in the next section. All complexes display irreversible oxidations at potentials between +1.00 V and +1.79 V, which could be tentatively assigned to oxidation of the chloride counter ion,²⁵ as well as oxidation of the phenolate ring (for **2a**,**b** and **3a**, **b**).²⁶

If one considers the pKa of phenol of 10.0 compared with the pKa of 2- picolinic acid at 1.07, it is clear that the latter is much more acidic meaning that the conjugate base is more stable and thus a weaker donor. A weaker donor, in turn, should be less able to stabilize a higher oxidation state of a bound metal, leading to the observed higher oxidation potentials for the 2-carboxyphen and 2-carboxybpy complexes **4** and **5** (see pages S2-S9 for experimental details).

Water oxidation catalysis

The complexes 2a and 4 were tested for their ability to catalyze water oxidation in the presence of ceric ammonium nitrate (CAN) as a sacrificial electron acceptor in aqueous nitric acid (10 mL, pH = 1). Given the steric advantage of the 6,5 chelation in 2a compared to the 5,5 chelation in 4, we expected a difference in activity for the two systems. Curiously, almost superimposable oxygen evolution curves were obtained for both catalysts as can be seen in Figure 1A (black and red lines for 2a and 4, respectively). The oxygen evolution was rapid

ACS Catalysis

during the first 2 hours after which it declined gradually. A kinetic study was carried out (Figure 1B) and an initial rate of oxygen evolution of 0.13 s^{-1} was measured for catalyst **2a**. This value is marginally less than the 0.15 s⁻¹ measured for catalyst **4**.

To help better understand the catalyzed oxidation process, we examined the ESI mass spectra of **2a** in presence of increasing equivalents of CAN. We noticed that with 8 equivalents of CAN a cluster of mass signals at m/z = 558.14 emerged (Figure S4), whose mass value and profile corresponded to the mass signals of the [**4**]⁺ cation (m/z = 558.05). It appeared that the phenoxide portion of **2a** had been destroyed by oxidation. Such oxidation would likely proceed through the formation of a *p*-benzoquinone-type intermediate that could further oxidize to a COOH substituent.²⁷⁻²⁸ The huge excess of CAN (10,000 equivalents) over **2a** would result in an instantaneous conversion to **4**, explaining the identical O₂ evolution curves in Figure 1A.



Figure 1. A: O_2 evolution versus time and corresponding TON plots for catalysts **4** (red line), **2a** (black line) and **2b** (green line). Conditions: 20 µM catalyst and 0.2 M CAN in 10 mL HNO₃ (pH = 1.0). B: Initial rate of O_2 evolution versus concentrations of catalysts.

These preliminary results suggest that CAN serves a dual purpose: it promotes ligand oxidation of the pre-catalyst (**2a**), and acts as a sacrificial oxidant for the actual catalyst (presumably **4**), which generates O₂. To gain further insight, we initiated a methodical investigation of this unusual process. We first synthesized and examined the catalytic activity of the methyl-substituted derivative **2b**. It was expected that a 4-methyl substituent on the phenoxy ring would impede ligand oxidation. Indeed **2b** still functioned as a WOC but generated lesser

quantities of oxygen (Figure 1A, green line) at a considerably slower initial rate (0.06 s⁻¹, Figure 1B). We then examined the reaction using a higher catalyst concentration (0.2 mM) for each of the phen-based systems, **2a**, **2b**, and **4**. In contrast to the activity seen at 0.02 mM (Figure 1A), a slight difference in gas evolution (both initial and final) could be observed between **4** and **2a** (Figure S5A). This difference became significant upon using an even higher catalyst concentration (2 mM) (Figure 2A). If we consider that each molecule of oxygen will require the removal of 4 electrons by 4 CAN molecules, 10 mL of a 0.2 M CAN solution can theoretically produce 500 μ mol of oxygen. In Figure 2A we observe the generation of 410 μ mol by the catalyst **4** and the abrupt halting of the reaction after less than 10 minutes. For catalyst **2a** we observe a slower rate and the production of lesser quantities of gas (320 μ mol). The less reactive methyl-substituted catalyst **2b** produces the same amount but at an even slower rate.

This drastic change in behavior at higher catalyst concentrations can be explained by taking into account the relative concentration of the sacrificial oxidant. Compared to the initial catalytic conditions (Figure 1A), there are now lesser equivalents of CAN (100 - 1000 eq.) per catalyst. The apparent consumption of CAN during ligand oxidation and catalyst conversion into **4** creates a further deficit of the oxidant. This limits the overall O_2 evolution reaction, resulting in the lower gas evolution from reactions containing **2a** and **2b**. This was further illustrated by pretreating **2a**,**b** with 8 equivalents of CAN and subjecting them to the conditions used in Figure S5A. A slight improvement in performance was observed in terms of initial rate and overall O_2 evolution. However the difference in activity compared to **4** still persists (Figure S5B), indicating that excess CAN is necessary for complete conversion of **2a** into **4**.





Figure 2. Results from water oxidation studies using catalysts **2a**, **2b** and **4** (2 mM each) in presence of 0.2 M CAN, in aqueous HNO₃ (pH = 1). **A:** Gas evolution traces for catalysts **4** (red line), **2a** (black line) and **2b** (green line). **B:** Chromatograms from GC analysis illustrating the presence of CO_2 in the reaction headspace of catalysts **2a** and **2b**.

Curiously enough, while **4** and **2b** demonstrate an increase in gas evolution upon changing catalyst concentration from 0.2 mM to 2 mM, no further increase was observed for **2a** (Table S3). Additionally, as noted previously, both **2a** and **2b** evolve the same amount of gas at a 2mM concentration. These results are again a consequence of the structural difference between **2a**,**b** (since the relatively quicker conversion of **2a** into **4** consumes CAN much faster than **2b**), and clearly suggest that at high catalyst concentrations, the activity is CAN limited.

We analyzed the head space gas at the end of the catalytic reaction (at 2mM catalyst concentration) using a Porapak Q gas chromatography column and a thermal conductivity detector. We found that CO_2 was generated in the reaction of **2a** and to a lesser extent in the reaction of **2b**, but no CO_2 was generated in the reaction of **4** (Figure 2B). We also investigated the behavior of the free ligands **10a,b** and 2-carboxyphen (**14**) in the presence of CAN. Similar

to their respective complexes, ligand **10a** with the 2-phenoxy substituent showed much higher quantities of CO_2 evolution than ligand **10b** with the 4-methylphenoxy group. The 2-carboxyphen ligand **14** did not show any evidence of CO_2 formation (Figure S6). All these results further suggest degradation taking place only in the 2-phenoxy-based compounds. Since other undetectable oxidation products may also be formed, it is difficult to quantify these CO_2 evolution experiments.

Treatment of the reaction solutions with KPF₆ after water oxidation allowed precipitation and isolation of the catalysts. ¹H-NMR of these solids recovered from the reactions of **2a** and **2b** revealed them to be identical to **4** (Figure S7). Additionally, ESI analysis of the solids revealed the disappearance of the expected m/z peaks for catalysts **2a** (Figure 3A) and **2b** (Figure 3B) and the presence of the peak belonging to the [**4**]⁺ cation instead, clearly indicating that both phenoxy-based complexes undergo a transformation to **4** through ligand oxidation. Consistent with the GC and ¹H-NMR analysis, complex **4** did not appear to undergo any change in its original structure after the reaction (Figure S8), highlighting its robustness.



Figure 3. ESI-MS (CH₃OH as solvent) of A) catalyst **2a** and B) catalyst **2b** before and after water oxidation, depicting conversion to catalyst **4**.

As was mentioned earlier, Sun and coworkers examined water oxidation catalysis involving Ru(II) complexes of 6,6'-dicarboxybpy and 2,9-dicarboxyphen.²³ They observed very different behavior between these two closely related complexes with the dicarboxybpy system showing remarkably high activity in water oxidation. For this reason we decided to examine the series of complexes **3a**, **3b**, and **5** which are simply bpy analogs of the series **2a**, **2b**, and **4**. The bpy compounds were prepared in a manner directly analogous to the method used for the phen series as outlined in Scheme 1. When tested for water oxidation using CAN as the sacrificial reagent, under the same conditions (see Figure 1) as were initially employed for the phen catalysts, all three bpy complexes, **3a**, **3b**, and **5** were essentially inactive (Figure S9). If the experiment is repeated at 100-fold higher concentration of the catalyst, similar to what is shown in Figure 2, gas evolution is observed (Figure 4) but CO_2 is also observed in all three cases. After gas evolution ceases, an attempt was made to recover and identify the depleted catalyst by adding KPF₆ to precipitate the complex. Dark insoluble material was observed and is believed to be the result of decomposition of the catalyst.





Figure 4. Results from water oxidation experiments carried out at higher catalyst concentrations (2.5 mM) with CAN (0.2 M) in aq. HNO₃. A) O_2 evolution curves. B) Corresponding gas chromatograms, depicting presence of CO_2 in the headspace.

This inconsistent catalytic behavior of **3a**, **b** and **5** suggests that decay of the catalyst may be a competing pathway. Therefore, even though the rate of decay is slow it may be comparable to the rate of O_2 evolution, especially in the presence of a large excess of CAN. At low concentration of **3a**, **b** and **5**, the catalyst rapidly decomposes and loses activity before very much O_2 evolution can be detected (see Figure S9). Accordingly, at higher concentrations of catalyst, water oxidation can compete with catalyst decay. To investigate further, the catalytic activity of **5** was compared to the well-known analog [Ru(tpy)(bpy)H₂O]^{2+ 18}. The latter was found to generate much more O_2 than **5** at lower concentrations, where catalyst **5** was essentially inactive (Figure S10). These results suggests that the low activity of **5** (and **3a**,**b**) probably results from the poor rate of water binding to the metal center, leaving the catalysts prone to oxidative degradation.

Based on the experimental evidence, the carboxyphen complex 4 does not appear to decompose readily upon treatment with CAN. As shown at the top of Figure 2B, essentially no CO_2 is detected in the headspace after reaction. By contrast, the carboxybpy complex 5 seems to

Page 13 of 22

ACS Catalysis

undergo decomposition as evidenced by CO_2 formation (Figure 4). One could imagine that the bpy moiety might be more prone to oxidative decomposition since the two pyridine rings are connected only by a σ -bond while a fused central benzo ring unites the two pyridine moieties in phenanthroline. Oxidative decomposition of phen usually involves oxidation of the C5-C6 bridging bond to first give a quinone that in turn oxidizes to a 3,3'-dicarboxybpy.²⁹ One might imagine ways in which 5,6-substitution on phen might slow down this oxidative decay.

A successful water oxidation catalyst is one that consumes the entire sacrificial reagent (CAN) before the catalyst itself is destroyed by the strongly oxidizing conditions. We examined this interplay between the catalyst (4) and CAN concentration in three parallel experiments where the CAN concentration was kept constant at 0.2 M and the catalyst concentration was varied from 50 μ M - 1 mM. Each experiment was run in duplicate and when oxygen evolution had essentially stopped, more catalyst was added to one flask and more CAN was added to the other. For the run at lowest catalyst concentration (50 μ M), about 200 μ mol of oxygen were produced after 5 hours. All the catalyst had been consumed so that the addition of excess CAN had no effect but the addition of catalyst caused the resumption of oxygen evolution at a somewhat slower rate (Figure 5A). With a 20-fold increase in the catalyst concentration, the reaction produced about 350 µmol of oxygen after 15 minutes. In this run all the CAN had been consumed so that the addition of more catalyst had no effect while the addition of more CAN caused oxygen evolution to resume (Figure 5C). In the intermediate experiment where the catalyst concentration was 0.25 mM, both the catalyst and CAN were consumed (or destroyed) in 2 hours and the addition of either species independently did not result in more oxygen evolution (Figure 5B). These results help assign an optimal CAN/catalyst ratio (800:1, Figure 5B) where the effects of degradation balance out, and also ascertain that the reactions are catalyst or CAN limited, depending on the deviation from this optimal CAN/catalyst ratio.





Figure 5. Effect of addition of excess catalyst 4 and CAN on O_2 evolution, at different initial catalyst concentrations. Initial conditions: [Cat] + CAN (0.2 M) in aq. HNO₃ (10 mL, pH = 1). All reactions involved addition of 1 mmol of CAN (red dotted lines) along with addition of the catalyst (solid red lines) after the pressure traces ceased to increase. A sharp pressure increase is always observed at the time of addition.

Six versus 7-coordination: mechanistic considerations

If a six-coordinate metal complex such as 4 is going to hydrate the metal center by forming a Ru-OH₂ bond, the system must either loose a ligand or become 7-coordinate. The geometry required by a 7-coordinate species is pentagonal bipyramid. In the case of 4 a pentagonal bipyramid would be highly distorted and hence rather unlikely. When complex 4 in D₂O is acidified by D_2SO_4 the ¹H NMR spectrum changes somewhat indicating that protonation of the carboxylic acid has occurred. Nevertheless, the five protons on the tpy ligand that integrate for 2H apiece continue to integrate for 2H in the protonated complex, indicating that C_s geometry has been retained (Figure 6). The implication for the reaction of 4 is that protonation must occur

on the carboxy group which then dissociates from the metal center and is replaced by a water molecule.



Figure 6. ¹H NMR of 4(Cl) in (a) D_2O and (b) D_2O containing 0.05 M D_2SO_4 . Marked peaks with integral of 2H are assigned to the tpy ligand of 4(Cl) and indicate C_s symmetry.

The hydration and Ru oxidation processes are clearly evidenced by comparison of observed and calculated mass spectrum signals as illustrated in Figure 7. The peak centered at 557.97 can be assigned to $[4]^+$ (m/z = 558.05). Loss of one electron to Ce^{IV} and the addition of H₂O gives a peak at 287.93 that corresponds to $[4 + H_2O]^{2+}$ (m/z = 288.03). Finally the loss of a second electron and two protons gives a peak at 574.05 that corresponds to $[4 + O]^+$ (m/z = 573.97). It should be noted that the detection conditions of the mass spectrometer are different from the catalytic O₂-evolving conditions. Protonation of the $[4 + O]^+$ species cannot be excluded in very acidic aqueous solution.



Figure 7. Observed and calculated mass spectrum signals of ruthenium-containing species after treatment of 4(Cl) with one and two equivalents of CAN.

The possibility of hydrogen-bonding interactions taking place between a water molecule and the bound carboxylic acid was demonstrated by X-ray crystal structure determination. Figure 8 shows well organized octahedral behavior for **4** along with a water molecule H-bonded to the carboxy substituent. The single counterion (triflate) supported a Ru(II) structure. The outer Ru-N bonds for the tpy ligand were slightly longer than the inner Ru-N bond and the Ru-O bond was even longer at 2.15 Å. The bond between this same oxygen and C16 is longer (1.29 Å) than the O2-C16 bond (1.24 Å), indicating more carbonyl character in the latter bond. The interior angles around Ru were all similar with the angle involving the phen ring (79.90 °) being slightly larger. The dihedral angles are small and consistent with planar ligand structures (Table 2).



Figure 8. Thermal ellipsoid plot representation of crystal structures of 4(OTf) at 50% probability; non-polar hydrogen atoms, fractional solvent and counter ions are omitted for clarity.

1

ACS Catalysis

-	
- 2	
_	
- 3	
- 4	
_	
-5	
~	
6	
_	
- 7	
~	
- 8	
~	
-9	
	~
1	0
1	1
	-
1	2
	_
1	3
1	4
	_
1	5
	-
1	6
	_
1	1
,	~
1	8
	~
1	9
_	-
2	0
-	ĩ
2	1
_	
- 2	2
-	-
2	3
~	0
- 2	4
-	
2	5
~	U
- 2	6
-	0
2	7
~	
2	8
~	U
2	a
~	J
િર	\cap
J	U
2	1
J	
2	2
5	2
2	3
J	5
2	Λ
5	4
2	Б
5	J
2	6
3	0
2	7
0	1
2	Q
0	0
2	٥
3	Э
Λ	Λ
-	U
Δ	1
-	
Δ	2
-	<u>~</u>
Δ	3
-	U
Δ	4
-	Τ.
Δ	5
-	J
Δ	6
-	0
Δ	7
-	'
Δ	8
-	0
Δ	q
-	J
5	0
J	0
5	1
J	
5	2
0	-
5	3
0	9
5	4
0	r
5	5
J	0
5	6

57 58

59 60 **Table 2.** Selected bond lengths (Å), bond angles (°), and dihedral angles (°) for crystal structure of **4**(OTf)

Bond distance (Å)	
Ru1–O1	2.146(1)
Ru1–N1	2.070(1)
Ru1–N2	1.969(1)
Ru1–N3	2.059(1)
Ru1–N4	1.979(1)
Ru1–N5	2.060(1)
O1-C16	1.289(2)
O2-C16	1.241(2)
O2-H1WA	1.969(3)
O1-H2WA	4.175
Bond an	ngles (°)
O1-Ru1-N4	76.39(4)
N1-Ru1-N2	79.30(5)
N2-Ru1-N3	79.33(5)
N4-Ru1-N5	79.90(5)
Dihedral	angles (°)
01-C16-C17-N4	2.5(2)
O1-C16-C17-N4 N4-C21-C25-N5	2.5(2) 1.1(2)
O1-C16-C17-N4 N4-C21-C25-N5 N2-C10-C11-N3	2.5(2) 1.1(2) 1.0(2)

A theoretical study provides more insight on the specific interaction between complex 4 in the trivalent oxidation state and water. We considered two possible coordination events of water where either the carboxylate or a pyridyl is decoordinated. After testing different structures of potential Ru^{III}-aqua isomers, we conclude that 4_{ag}^{2+} (Scheme 3) is the most stable Ru^{III}-aqua species, in which the carboxylate group dissociates from the metal center and forms a hydrogenbonded network with ligated and solvated water molecules. In another scenario where pyridyl is replaced by water, the resulting aqua species is ca 13 kcal/mol higher in free energy than 4_{aq}^{2+} (Figure S11). The free energy of 4_{aq}^{2+} is slightly higher compared to 4^{2+} , indicating feasible equilibrium between these two species if the barrier between them is low. We then located transition states as well as intermediates in the 4^{2+} to 4_{ad}^{2+} conversion and indeed found a very low free energy barrier of merely 6.2 kcal/mol (Scheme 3), corresponding to a very fast rate of the carboxylate/aqua ligand exchange. Therefore, 4^{2+} and 4_{aq}^{2+} should exist in equilibrium in the aqueous solution. The importance of the hemilabile carboxylate ligand that facilitates water association has been observed for other ruthenium complexes.³⁰ It should be noted, however, that of 4^{2+} and 4_{aq}^{2+} only 4_{aq}^{2+} is capable of being oxidized to the Ru^{IV} state and the proposed active Ru^V state via proton coupled electron transfer (PCET) processes. A recent report demonstrating Fe-catalyzed water oxidation sheds light on an inner-sphere catalytic mechanism through the identification of an active $Fe^{IV}(O)(\mu - O)Ce^{IV}$ intermediate.³¹ As depicted earlier by *in-situ* ESI analysis of 4, the coordinatively saturated Ru^{IV}=O species is generated after addition of 2 equivalents of CAN (Figure 7), most likely proceeding via the transition states depicted below. Given the sterics of the entire process, the formation of a similar heterobimetallic adduct is highly improbable and thus CAN-driven oxidation of the Ru center most probably progresses via an outer-sphere mechanism.

ACS Catalysis



Scheme 3. Calculated pathway for carboxylate/water exchange in trivalent complex 4. Relative solvated free energies (brackets) are in kcal/mol. Bond distances of Ru–O(carboxylate) and Ru–O(aqua) are shown in Å.

CONCLUSIONS

A series of 2-hydroxphenyl derivatives of phen and bpy have been prepared using Suzuki coupling methodology. These molecules deprotonate the hydroxyl group to bind with Ru(II) as anionic ligands, forming a 6-membered chelate ring. When exposed to CAN in nitric acid (pH = 1), the parent phen system **2a** rapidly oxidizes to a 2-carboxyphen system **4** without further decay. This 2-carboxyphen complex shows good activity as a WOC, producing up to 80% of the theoretical amount of dioxygen. The incorporation of a methyl group on the phenol ring leads to **10b** and the corresponding Ru(II) complex **2b**. Methyl substitution slows down the ligand oxidation process but ultimately the same 2-carboxyphen system **4** is formed. An analogous series of complexes were prepared based on bpy rather than phen (**3a,b** and **5**). Contrary to what has been observed for a somewhat similar dicarboxybpy system, this series of complexes showed greatly diminished activity towards water oxidation under the same conditions used for the phenbased systems. An important lesson is that CAN is a powerful and sometimes selective oxidant, often leading to catalyst decomposition. More realistic results are likely to be obtained if the catalysts are activated by light rather than by CAN. However, in designing systems for

photochemical water oxidation, major focus must be on catalyst / photosensitizer stability to ensure high activity under the oxidative reaction conditions.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data for complex **4**(OTf), experimental details, ¹H NMR, mass and UV-vis spectra, gas chromatographs, oxygen evolution graphs, and a description of DFT calculations.

AUTHOR INFORMATION

Corresponding author

*Email for RT: thummel@uh.edu

Author contributions

[‡]These authors contributed equally.

ACKNOWLEDGMENTS

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-FG02-07ER15888, the Advanced Light Source supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, and the Robert A. Welch Foundation (Grant E-621).

REFERENCES

(1) Jafari, T.; Moharreri, E.; Amin, A. S.; Miao, R.; Song, W.; Suib, S. L. *Molecules* 2016, *21*, 900.
(2) Andreiadis, E. S.; Chavarot □ Kerlidou, M.; Fontecave, M.; Artero, V. *Photochem. Photobiol.* 2011, *87*, 946-964.
(3) Rüttinger, W.; Dismukes, G. C. *Chem. Rev.* 1997, *97*, 1-24.
(4) Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W. *Chem. Rev.* 2015, *115*, 12974-13005.
(5) Kärkäs, M. D.; Verho, O.; Johnston, E. V.; Åkermark, B. *Chem. Rev.* 2014, *114*, 11863-12001.
(6) Zong, R.; Thummel, R. P. *J. Am. Chem. Soc.* 2005, *127*, 12802-12803.
(7) Concepcion, J. J.; Jurss, J. W.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* 2008, *130*, 16462-16463.

1
2
3
4
5
6
7
0
0
9
10
11
12
13
14
15
16
17
10
10
19
20
21
22
23
24
25
20
20
21
28
29
30
31
32
33
34
35
20
30
37
38
39
40
41
42
43
11
44
40
46
47
48
49
50
51
52
53
5/
54
55
56
5/
58
59

60

(8) Masaoka, S.; Sakai, K. Chem. Lett. 2009, 38, 182-183.

- (9) Duan, L.; Xu, Y.; Gorlov, M.; Tong, L.; Andersson, S.; Sun, L. Chem. Eur. J. 2010, 16, 4659-4668.
- (10) Tong, L.; Thummel, R. P. Chem. Sci. 2016, 7, 6591-6603.
 - (11) Limburg, B.; Bouwman, E.; Bonnet, S. ACS Catal. 2016, 6, 5273-5284.
- (12) Limburg, B.; Bouwman, E.; Bonnet, S. Coord. Chem. Rev. 2012, 256, 1451-1467.
- (13) Corbucci, I.; Ellingwood, K.; Fagiolari, L.; Zuccaccia, C.; Elisei, F.; Gentili, P. L.;
- Macchioni, A. Catal. Today 2016, in press, http://dx.doi.org/10.1016/j.cattod.2016.10.030
 - (14) Hong, D.; Murakami, M.; Yamada, Y.; Fukuzumi, S. *Energy Environ. Sci.* **2012**, *5*, 5708-5716.
 - (15) Polyansky, D. E.; Muckerman, J. T.; Rochford, J.; Zong, R.; Thummel, R. P.; Fujita, E. *J. Am. Chem. Soc.* **2011**, *133*, 14649-14665.
 - (16) Concepcion, J. J.; Tsai, M.-K.; Muckerman, J. T.; Meyer, T. J. J. Am. Chem. Soc. **2010**, *132*, 1545-1557.
 - (17) Yan, L.; Zong, R.; Pushkar, Y. J. Catal. 2015, 330, 255-260.
 - (18) Pushkar, Y.; Moonshiram, D.; Purohit, V.; Yan, L.; Alperovich, I. J. Am. Chem. Soc. 2014, 136, 11938-11945.
 - (19) Tseng, H.-W.; Zong, R.; Muckerman, J. T.; Thummel, R. *Inorg. Chem.* **2008**, *47*, 11763-11773.
 - (20) Kaveevivitchai, N.; Kohler, L.; Zong, R.; El Ojaimi, M.; Mehta, N.; Thummel, R. P. *Inorg. Chem.* **2013**, *52*, 10615-10622.
 - (21) Kärkäs, M. D.; Åkermark, B. Chem. Rec. 2016, 16, 940-963.
 - (22) Duan, L.; Wang, L.; Li, F.; Li, F.; Sun, L. Acc. Chem. Res. 2015, 48, 2084-2096.
 - (23) Tong, L.; Duan, L.; Xu, Y.; Privalov, T.; Sun, L. Angew. Chem. Int. Ed. 2011, 50, 445-449.
 - (24) Norrby, T.; Börje, A.; Åkermark, B.; Hammarström, L.; Alsins, J.; Lashgari, K.; Norrestam, R.; Mårtensson, J.; Stenhagen, G. *Inorg. Chem.* **1997**, *36*, 5850-5858.
 - (25) Wickramasinghe, L. D.; Zhou, R.; Zong, R.; Vo, P.; Gagnon, K. J.; Thummel, R. P. J. Am. *Chem. Soc.* **2015**, *137*, 13260-13263.
 - (26) Iniesta, J.; Michaud, P.; Panizza, M.; Cerisola, G.; Aldaz, A.; Comninellis, C. *Electrochim. Acta* **2001**, *46*, 3573-3578.
 - (27) Sridharan, V.; Menéndez, J. C. Chem. Rev. 2010, 110, 3805-3849.
 - (28) Li, X.-Y.; Cui, Y.-H.; Feng, Y.-J.; Xie, Z.-M.; Gu, J.-D. Water Res. 2005, 39, 1972-1981.
 - (29) Eckhard, I.; Summers, L. Aust. J. Chem. 1973, 26, 2727-2728.
 - (30) Wang, Y.; Duan, L.; Wang, L.; Chen, H.; Sun, J.; Sun, L.; Ahlquist, M. S. *ACS Catal.* **2015**, *5*, 3966-3972.
 - (31) Codolà, Z.; Gómez, L.; Kleespies, S. T.; Que, L., Jr.; Costas, M.; Lloret-Fillol, J. *Nat. Commun.* **2015**, *6*, 5865.

Table of contents graphic

