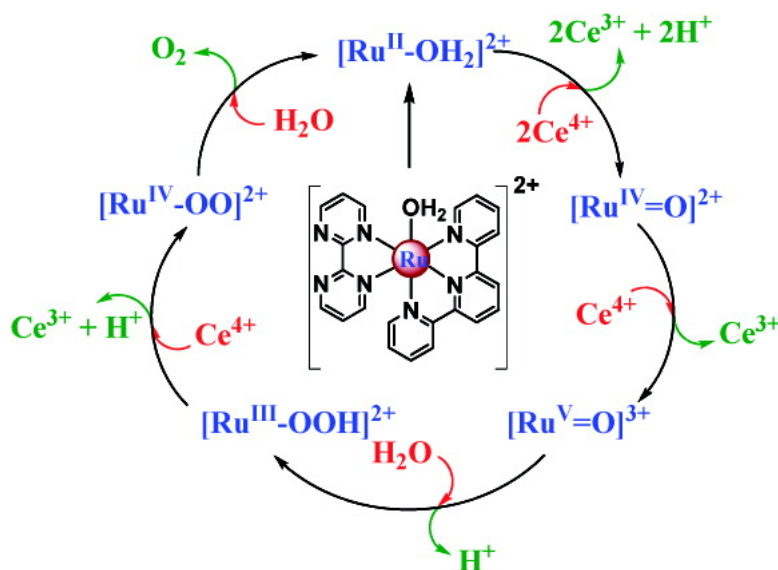## Communication

# One Site is Enough. Catalytic Water Oxidation by [Ru(tpy)(bpm)(OH)] and [Ru(tpy)(bpz)(OH)]

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# One Site is Enough. Catalytic Water Oxidation by [Ru(tpy)(bpm)(OH$_2$)]$^{2+}$ and [Ru(tpy)(bpz)(OH$_2$)]$^{2+}$

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In natural photosynthesis, and many schemes for artificial photosynthesis, water oxidation, $2H_2O \rightarrow O_2 + 4e^- + 4H^+$, is a key step.[1,2] A number of molecular catalysts have been reported for this reaction[2−8] but little mechanistic information is available. A detailed, medium-dependent mechanism for water oxidation by the blue Ru dimer *cis,cis*-[(bpy)$_2$(H$_2$O)Ru$^{III}$ORu$^{III}$(OH$_2$)(bpy)$_2$]$^{4+}$ (bpy is 2,2′-bipyridine) was reported recently. In 0.1 M HNO$_3$, under catalytic conditions with excess Ce(IV), rapid oxidation occurs through the intermediate [(O)Ru$^V$−O−Ru$^V$(O)]$^{4+}$ to give a second intermediate tentatively identified as the peroxide, [(bpy)$_2$(O)RuO-Ru(OOH)(bpy)$_2$]$^{4+}$.[2] A peroxidic intermediate has also been proposed in water oxidation at the Mn$_4$Ca cluster in the oxygen evolving complex (OEC) of photosystem II.[9,10]

A significant question remains as to whether or not dimeric or higher order structures are required to achieve catalytic water oxidation. Qualitative evidence for water oxidation by monomeric complexes of Ir and Ru has been presented by Bernhard, et al. and by Thummel, et al., respectively.[4,7] We report here sustained catalytic water oxidation upon oxidation of the monomeric complexes [Ru(tpy)(bpm)(OH$_2$)]$^{2+}$ and [Ru(tpy)(bpz)(OH$_2$)]$^{2+}$ (tpy is 2,2′:6′,2″-terpyridine; bpm is 2,2′-bipyrimidine; bpz is 2,2′-bipyrazine) by a well defined mechanism involving Ru(V).

Reaction of [Ru(tpy)(C$_2$O$_4$)(OH$_2$)]$^{11}$ with bpz or bpm in 0.1 M HClO$_4$ or of [Ru(tpy)(L)(Cl)]$^+$ (L is bpm or bpz) with AgNO$_3$ in 1:1 H$_2$O/MeOH yields the corresponding aqua complexes [Ru-(tpy)(bpz)(OH$_2$)]$^{2+}$ and [Ru(tpy)(bpm)(OH$_2$)]$^{2+}$. They are analogues of [Ru(tpy)(bpy)(OH$_2$)]$^{2+}$ and *cis*-[Ru(bpy)$_2$(py)(H$_2$O)]$^{2+}$ (py is pyridine) which, when oxidized to their Ru$^{IV}$=O forms, have an extensive stoichiometric and catalytic oxidative reactivity toward a variety of organic and inorganic molecules.[12]

As shown in Figure 1, the bpm complex shares with [Ru(tpy)(b-py)(OH$_2$)]$^{2+}$ multiple, pH-dependent oxidations in aqueous solutions. For [Ru(tpy)(bpy)(OH$_2$)]$^{2+}$, pH dependent Ru$^{III}$/Ru$^{II}$ and Ru$^{IV}$/Ru$^{III}$ couples appear separated by 92 mV over a broad pH range characteristic of closely spaced Ru(III/II) and Ru(IV/III) couples. The small potential separation between couples is a consequence of "redox potential leveling" and the PCET nature of the couple.[2,13] Protons are lost with no build up of charge between couples, and higher oxidation state Ru(IV) is stabilized by Ru=O bond formation. There is no evidence for further oxidation of this complex to the solvent limit at ∼1.8 V, and it is not a catalyst for water oxidation.

For [Ru(tpy)(bpm)(OH$_2$)]$^{2+}$, Ru$^{III}$ is a "missing" oxidation state.[2,12,13] A single 2e$^-$ Ru$^{IV}$/Ru$^{II}$ wave, as shown by peak current comparisons with the [Ru(bpy)$_3$]$^{3+/2+}$ couple, is observed from pH = 0 to pH = 14 with a change from the [Ru$^{IV}$=O]$^{2+}$ + 2e$^-$ + 2H$^+$ → [Ru$^{II}$−OH$_2$]$^{2+}$ couple to [Ru$^{IV}$=O]$^{2+}$ + 2e$^-$ + H$^+$ → [Ru$^{II}$−OH]$^+$, past p$K_{a,1}$ = 9.7. $E_{1/2}$ for the Ru$^{IV}$/Ru$^{III}$ couple is lower than $E_{1/2}$ for the Ru$^{III}$/Ru$^{II}$ couple owing to bpm stabilization of Ru(II) by backbonding and stabilization of Ru(IV) (and Ru(V), see below) by σ donation.[14,15]
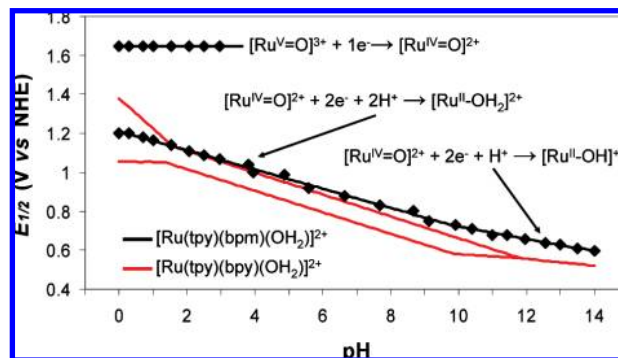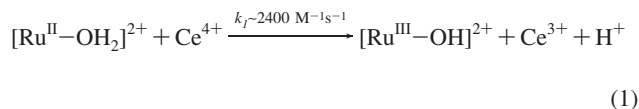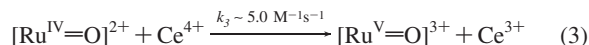


**Figure 1.** Plots of $E_{1/2}$ (V vs NHE) vs pH for the Ru(V/IV) and Ru(IV/II) redox couples of [Ru(tpy)(bpm)(OH$_2$)]$^{2+}$ and for the Ru(IV/III) and Ru(III/II) redox couples of [Ru(tpy)(bpy)(OH$_2$)]$^{2+}$ in aqueous solution ($I$ = 0.1 M; $T$ = 298 K; glassy carbon working electrode).

At higher potentials a pH-independent, 1e$^-$ wave appears in the cyclic voltammogram at 1.65 V as a shoulder on the onset of a catalytic wave for water oxidation, Figure S6. The electrochemistry for [Ru(tpy)(bpz)(OH$_2$)]$^{2+}$ is similar to that for [Ru(tpy)(bpm)-(OH$_2$)]$^{2+}$ with redox potentials for the corresponding Ru(IV/II) and Ru(V/IV) couples shifted to higher potentials (Figure S5 and S6, Supporting Information).

Oxidation to Ru(V) triggers water oxidation both electrochemically and with added Ce(IV). Addition of 2 equiv of Ce(IV) to a solution of [Ru$^{II}$(tpy)(bpm)(OH$_2$)]$^{2+}$ in 0.1 M HNO$_3$ ($\lambda_{max}$ = 485, 364, 331 (sh), and 309 nm) results in formation of [Ru$^{IV}$(tpy)-(bpm)(O)]$^{2+}$ ($\lambda_{max}$ = 430 (sh), 353 (sh), 336, and 324 nm) with $k$(25 °C) ≈ 2400 M$^{-1}$ s$^{-1}$ (eqs 1 and 2).

$$[Ru^{II}-OH_2]^{2+} + Ce^{4+} \xrightarrow{k_1 \sim 2400 \text{ M}^{-1}\text{s}^{-1}} [Ru^{III}-OH]^{2+} + Ce^{3+} + H^+$$

(1)

$$[Ru^{III}-OH]^{2+} + Ce^{4+} \xrightarrow{\text{rapid}} [Ru^{IV}=O]^{2+} + Ce^{3+} + H^+ \quad (2)$$

Further addition of 1 equiv of Ce(IV) to [Ru$^{IV}$=O]$^{2+}$, or 3 equiv of Ce(IV) to [Ru$^{II}$(OH$_2$)]$^{2+}$, results in formation of [Ru$^V$=O]$^{3+}$, $k$(25 °C) ≈ 5.0 M$^{-1}$ s$^{-1}$ (eq 3), but as a transient.

$$[Ru^{IV}=O]^{2+} + Ce^{4+} \xrightarrow{k_3 \sim 5.0 \text{ M}^{-1}\text{s}^{-1}} [Ru^V=O]^{3+} + Ce^{3+} \quad (3)$$

As shown by UV−visible spectral changes over time, Figure S8, it undergoes a further reaction with water to give a second intermediate which we tentatively formulate as the peroxido complex, [Ru$^{III}$(tpy)(bpm)(OOH)]$^{2+}$ ([Ru$^{III}$(OOH)]$^{2+}$) (eq 4). The peroxidic complex decomposes on a time scale of minutes to give [Ru$^{II}$−OH$_2$]$^{2+}$ and, presumably, O$_2$, Figure S9. In a redox titration between 2 and 3 equivs of Fe$_{aq}$$^{2+}$ were consumed per
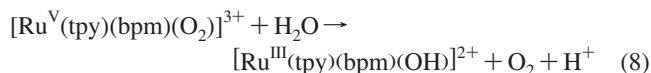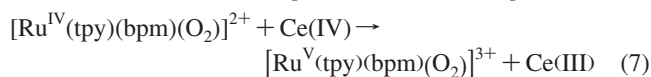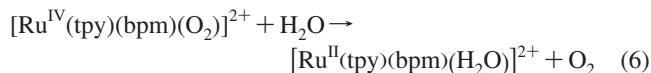
$[Ru^{III}(OOH)]^{2+}$ consistent with partial decomposition following its relatively slow formation by Ce(IV) oxidation. Both the decomposition reaction and further characterization of the intermediate are currently under investigation.

Under catalytic conditions with 30 equiv of $Ce^{IV}$ added, $[Ru^{III}(tpy)(bpm)(OOH)]^{2+}$ undergoes further oxidation to an additional intermediate which we tentatively assign as the $Ru^{IV}$ peroxide $[Ru^{IV}(tpy)(bpm)(O_2)]^{2+}([Ru^{IV}OO]^{2+})$ (eq 5).

$$[Ru^{V}(tpy)(bpm)(O)]^{3+} + H_2O \rightarrow$$
$$[Ru^{III}(tpy)(bpm)(OOH)]^{2+} + H^+ \quad (4)$$

$$[Ru^{III}(tpy)(bpm)(OOH)]^{2+} + Ce(IV) \rightarrow$$
$$[Ru^{IV}(typ)(bpm)(O_2)]^{2+} + Ce(III) + H^+ \quad (5)$$

Based on the results of DFT calculations on $[Ru^{IV}(tpy)\text{-}(bpm)(O_2)]^{2+}$, a seven-coordinate structure with a bidentate peroxido ligand is favored over a six-coordinated structure with a terminal peroxido ligand. All crystallographically characterized $[Ru^{IV}(O_2)]^{n+}$ complexes display this seven-coordinate structure.[16,17]

Under catalytic conditions with 30 equiv of Ce(IV) in 0.1 M $HNO_3$, $[Ru^{IV}OO]^{2+}$, with $\lambda_{max} = 436$, 358 (sh), 339 (sh), 316 (sh), and 286 nm, dominates at the catalytic steady state. Loss of Ce(IV) monitored at 360 nm is zero order in Ce(IV) and first order in complex with $k(25\ ^\circ C) = 7.5 \times 10^{-4}\ s^{-1}$ (Figures S11 and S12), consistent with decomposition of $[Ru^{IV}OO]^{2+}$ as the rate limiting step (eq 6). In 1.0 M $HNO_3$ the kinetics of Ce(IV) loss are significantly enhanced and mixed first and second order in character. As shown in eq 7, this is consistent with further oxidation of $[Ru^{IV}OO]^{2+}$ by Ce(IV) competing with the first order pathway in eq 6. Subsequent water oxidation presumably occurs by eq 8 followed by reoxidation of Ru(III). The appearance of the Ce(IV) pathway is a consequence of the enhanced $E^{\circ\prime}$ for the Ce(IV/III) couple at higher acid concentrations.[18] Oxygen monitoring with an oxygen electrode in three separate experiments gave 100 ($\pm 3$)% of the expected $O_2$ after 7.5 turnovers (Figure S13).

$$[Ru^{IV}(tpy)(bpm)(O_2)]^{2+} + H_2O \rightarrow$$
$$[Ru^{II}(tpy)(bpm)(H_2O)]^{2+} + O_2 \quad (6)$$

$$[Ru^{IV}(tpy)(bpm)(O_2)]^{2+} + Ce(IV) \rightarrow$$
$$[Ru^{V}(tpy)(bpm)(O_2)]^{3+} + Ce(III) \quad (7)$$

$$[Ru^{V}(tpy)(bpm)(O_2)]^{3+} + H_2O \rightarrow$$
$$[Ru^{III}(tpy)(bpm)(OH)]^{2+} + O_2 + H^+ \quad (8)$$

Initial results under catalytic conditions in 0.1 M $HNO_3$ with $[Ru(tpy)(bpz)(OH_2)]^{2+}$ as the catalyst gave closely related results with evidence for a $[Ru^{III}-OOH]^{2+}$ intermediate and an intermediate building up at the catalytic steady state with $\lambda_{max} = 385$ (sh), 359 (sh), 339 (sh), 316 and 284 (sh) nm. This intermediate is presumably the bpz analogue $[Ru^{IV}(tpy)(bpz)(O_2)]^{2+}$. Under catalytic conditions loss of Ce(IV) is also zero order in Ce(IV) with $k(25\ ^\circ C) = 1.4 \times 10^{-3}\ s^{-1}$ (eq 9). Based on redox potential measurements, water oxidation by $[Ru^{V}(tpy)(bpz)(O)]^{2+}$ is favored over the bpm complex with $E^{\circ\prime}(Ru^{V}=O^{3+}/Ru^{II}-OH_2^{2+}) \approx 1.42$ V (bpz) and 1.32 V (bpm) at pH = 1.

$$[Ru^{IV}(tpy)(bpz)(O_2)]^{2+} + H_2O \rightarrow$$
$$[Ru^{II}(tpy)(bpz)(H_2O)]^{2+} + O_2 \quad (9)$$
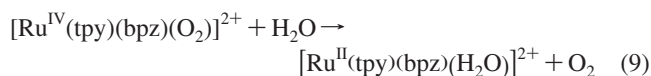
The mechanism for water oxidation catalysis by $[Ru(tpy)\text{-}(bpm)(OH_2)]^{2+}$ and $[Ru(tpy)(bpz)(OH_2)]^{2+}$ derived from our observations is shown in Figure 2. Notable is the use of single site catalysis and involvement of the $3e^-$ oxidized oxo complexes $[Ru^{V}(tpy)(bpm)(O)]^{3+}$ and $[Ru^{V}(tpy)(bpz)(O)]^{3+}$. Thermodynami-
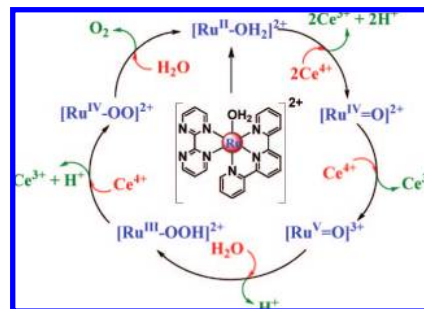


**Figure 2.** Proposed mechanism for water oxidation by the monomers $[Ru(tpy)(bpm)(OH_2)]^{2+}$ and $[Ru(tpy)(bpz)(OH_2)]^{2+}$ in 0.1 M $HNO_3$ or 0.1 M $HClO_4$.

cally, use of the higher oxidation state is advantageous with $\Delta G^{\circ\prime} = -0.90$ eV for water oxidation by $[Ru^{V}(tpy)(bpm)(O)]^{3+}$, $2[Ru^{V}=O]^{3+} + 3H_2O \rightarrow 2[Ru^{II}-OH_2]^{2+} + {}^3/_2 O_2 + 2H^+$ compared to $\Delta G^{\circ\prime} = +0.04$ eV for oxidation by Ru(IV), $2[Ru^{IV}=O]^{2+} + 2H_2O \rightarrow 2[Ru^{II}-OH_2]^{2+} + O_2$ (pH = 1). The appearance of peroxido intermediates is also a notable feature in the scheme. They are presumably high energy intermediates given $E^{\circ\prime} = 1.77$ V for the $H_2O_2/H_2O$ couple and $E^{\circ\prime} = -0.39$ V for $[Ru^{V}(tpy)(bpm)(O)]^{3+}$ oxidation of $H_2O$ to $H_2O_2$, $2[Ru^{V}=O]^{3+} + 6H_2O \rightarrow 2[Ru^{II}-OH_2]^{2+} + 3H_2O_2 + 2H^+$ at pH = 1.

Our results are important in establishing detailed mechanistic insight into water oxidation at a single ruthenium site and in paving the way toward a family of robust water oxidation catalysts.

**Supporting Information Available:** Detailed synthetic procedures, oxygen measurements, electrochemical and kinetic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

(1) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 6802–6827.
(2) Liu, F.; Concepcion, J. J.; Jurss, J. W.; Cardolaccia, T.; Templeton, J. L.; Meyer, T. J. *Inorg. Chem.* **2008**, *47*, 1727–1752.
(3) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029–4030.
(4) McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. *J. Am. Chem. Soc.* **2008**, *130*, 210–217.
(5) Betley, T. A.; Wu, Q.; Van Voorhis, T.; Nocera, D. G. *Inorg. Chem.* **2008**, *47*, 1849–1861.
(6) Tagore, R.; Crabtree, R. H.; Brudvig, G. W. *Inorg. Chem.* **2008**, *47*, 1815–1823.
(7) Zong, R.; Thummel, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 12802–12803.
(8) Deng, Z.; Tseng, H.-W.; Zong, R.; Wang, D.; Thummel, R. *Inorg. Chem.* **2008**, *47*, 1835–1848.
(9) Meyer, T. J.; Huynh, M. H. V.; Thorp, H. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5284–5304.
(10) Renger, G. *Photosynth. Res.* **2007**, *92*, 407–425.
(11) Adeyemi, S. A.; Dovletoglou, A.; Guadalupe, A. R.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 1375–1383.
(12) Meyer, T. J.; Huynh, M. H. V. *Inorg. Chem.* **2003**, *42*, 8140–8160.
(13) Huynh, M. H. V.; Meyer, T. J. *Chem. Rev.* **2007**, *107*, 5004–5064.
(14) Dovletoglou, A.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 4120–4127.
(15) Masllorens, E.; Rodriguez, M.; Romero, I.; Roglans, A.; Parella, T.; Benet-Buchholz, J.; Poyatos, M.; Llobet, A. *J. Am. Chem. Soc.* **2006**, *128*, 5306–5307.
(16) Navarro Clemente, M. E.; Juarez Saavedra, P.; Cervantes Vasquez, M.; Paz-Sandoval, M. A.; Arif, A. M.; Ernst, R. D. *Organometallics* **2002**, *21*, 592–605.
(17) Shen, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1998**, *17*, 3875–3882.
(18) Bondareva, T. N.; Stromberg, A. G. *Zh. Obsh. Khim.* **1955**, *25*, 666–671.

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