

Catalytic Water Oxidation by Ruthenium(II) Quaterpyridine (qpy) Complexes: Evidence for Ruthenium(III) qpy-*N,N'*-dioxide as the Real Catalysts**

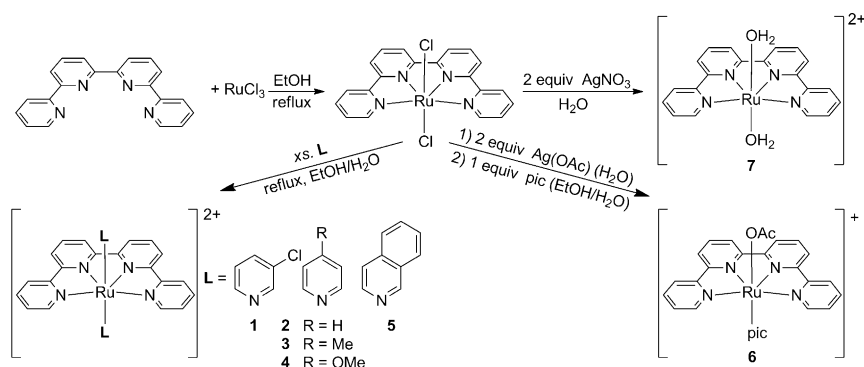
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Abstract: Polypyridyl and related ligands have been widely used for the development of water oxidation catalysts. Supposedly these ligands are oxidation-resistant and can stabilize high-oxidation-state intermediates. In this work a series of ruthenium(II) complexes $[\text{Ru}(\text{qpy})(\text{L})_2]^{2+}$ (qpy = 2,2':6',2'':6'',2''':6'''-quaterpyridine; L = substituted pyridine) have been synthesized and found to catalyze Ce^{IV} -driven water oxidation, with turnover numbers of up to 2100. However, these ruthenium complexes are found to function only as precatalysts; first, they have to be oxidized to the qpy-*N,N'*-dioxide (ONNO) complexes $[\text{Ru}(\text{ONNO})(\text{L})_2]^{3+}$ which are the real catalysts for water oxidation.

The four-electron oxidation of H_2O to O_2 is a key process in natural and artificial photosynthesis,^[1–3] and in recent years there have been considerable efforts in designing robust catalysts for this very important and complicated process.^[4,5] Since the discovery of the first water oxidation catalyst (WOC), $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}^{\text{III}}\text{ORu}^{\text{III}}(\text{OH})_2](\text{bpy})_2(\text{ClO}_4)_4$ (the “blue dimer”, bpy = 2,2'-bipyridine), by Meyer et al. in 1982,^[6a] a variety of ruthenium WOCs bearing pyridine-type ligands have been reported.^[6–11] Most ruthenium WOCs contain at least an aqua ligand or a labile ligand that can be replaced by water; the aqua complexes undergo proton-coupled electron transfer to generate active $\text{Ru}=\text{O}$ species. There are also a few six-coordinate ruthenium WOCs that bear only substitution-inert ligands but may form a seven-coordinate $\text{Ru}=\text{O}$

active intermediate.^[7b,8a,12] A notable example is $[\text{Ru}(\text{bda})(\text{L})_2]$ (bda = 2,2'-bipyridine-6,6'-dicarboxylate, L = pyridine and derivatives) reported by Sun et al., which can catalyze water oxidation with a high turnover frequency (TOF) of 300 s^{-1} and turnover number (TON) above 50 000.^[8c,d]

We recently discovered that a cobalt(II) complex bearing the 2,2':6',2'':6'',2''':6'''-quaterpyridine (qpy) ligand is an efficient catalyst for both water oxidation and reduction.^[13] Inspired by the work of Sun et al. we wanted to prepare six-coordinate ruthenium complexes based on qpy and pyridine ligands. Qpy is known to form metal complexes in *trans* configuration with a relatively large N-M-N bite angle,^[14] hence it may be possible to form a seven-coordinate $\text{M}=\text{O}$ species. We describe herein the synthesis and catalytic water oxidation by a series of ruthenium(II) complexes $[\text{Ru}(\text{qpy})(\text{L})_2]^{2+}$



Scheme 1. Synthetic routes for ruthenium complexes 1–7.

(Scheme 1). Polypyridyl ligands coordinated to ruthenium are generally believed to be reasonably stable under water oxidation conditions. However, we provide evidence that in catalytic water oxidation using $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (CAN) as terminal oxidant, the qpy ligand in $[\text{Ru}(\text{qpy})(\text{L})_2]^{2+}$ is first oxidized to a qpy-*N,N'*-dioxide (ONNO). The resulting complex $[\text{Ru}(\text{ONNO})(\text{L})_2]^{3+}$ is the real catalyst for water oxidation.

The synthesis of the ruthenium complexes is summarized in Scheme 1; complex 7 has been reported by Che et al.^[14] The structures of 3, 4, and 5 have been determined by X-ray crystallography. In 3, the ruthenium center adopts a distorted octahedral geometry with the equatorial positions occupied by the planar qpy ligand, and the axial positions by two

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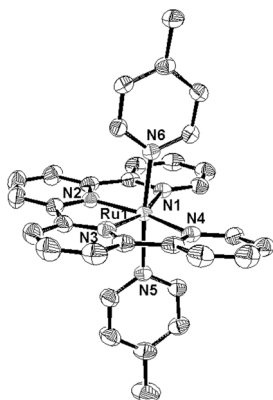


Figure 1. ORTEP plot of **3**. Thermal ellipsoids are drawn at 50% probability; anions, solvent, and hydrogen atoms are omitted for clarity.

picoline ligands (Figure 1 and Tables S1 and S2). The distances of the ruthenium center to the two outer pyridyl N atoms (Ru1–N1 2.132 Å, Ru1–N4 2.129 Å) are significantly longer (by 0.18 Å) than those to the inner pyridyl N atoms (Ru1–N2 1.946 Å, Ru1–N3 1.952 Å), due to considerable strain in the planar coordination mode of the qpy ligand. The X-ray structures of **4** and **5** are similar to that of **3** (Figure S1 and Tables S1 and S2).

Complexes **1–5** exhibit a reversible redox wave in cyclic voltammetry (CV) in H₂O/CH₃CN (3:1 v/v) at pH 1, which is assigned to the Ru^{III/II} couple (Table 1, Figure S2). The CV of **3** is shown in Figure 2. The $E_{1/2}$ values of **1–5** are similar to that of [Ru(bpy)₃]^{3+/2+} (1.02 V versus SCE).^[15] Complexes with electron-donating groups, such as **3** and **4**, have slightly lower $E_{1/2}$ than those with electron-withdrawing groups, such as **1**.

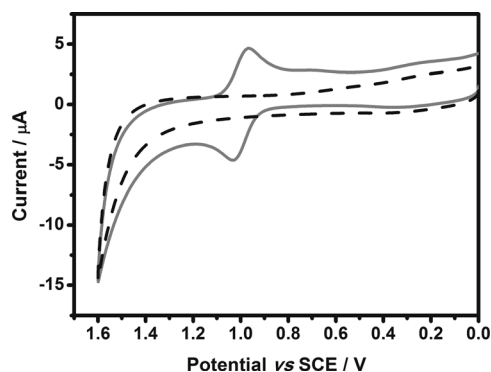


Figure 2. CV of **3** (0.5 mM, solid line) and blank (dashed line) at pH 1 in H₂O/CH₃CN (3:1 v/v). Scan rate = 100 mV s^{−1}.

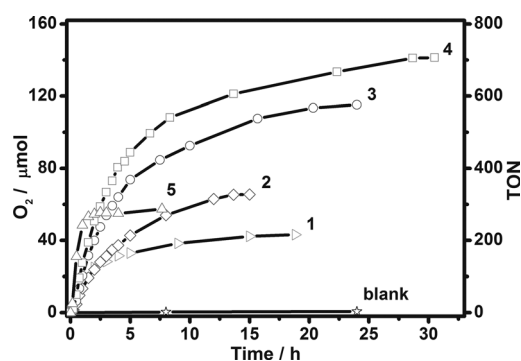


Figure 3. Plots of oxygen evolved and TON versus time for water oxidation by complexes **1–5** (25 μM) and CAN (247 mM) in 0.1 M HOTf (8.0 mL) containing CH₃CN (0.1 mL, to enhance solubility) at 25 °C. Oxygen was monitored by GC-TCD (TCD = thermal conductivity detector).

Table 1: Ru^{III/II} $E_{1/2}$ [V] and catalytic water oxidation data for complexes **1–5**.

Complex	$E_{1/2}$ [V] (ΔE [mV]) ^[a]	TON ^[b]	TOF _{max} [min ^{−1}] ^[c]
1	1.11 (58)	219	1.0
2	1.05 (58)	327	1.0
3	1.02 (56)	576	1.5
4	0.99 (56)	707	1.9
5	1.05 (62)	293	4.9

[a] Versus SCE. [b] Ruthenium complexes, 25 μM; CAN, 247 mM; T = 25 °C. TON = (mol of O₂)/(mol of catalyst). [c] The maximum TOF is calculated from the initial slope.

Although there is no catalytic current upon scanning to 1.6 V versus SCE in CV, oxygen evolution was readily observed for complexes **1–5** in water upon adding CAN (Figure 3 and Table 1). Complex **5** shows the highest TOF (4.9 min^{−1}), but it has a relatively low TON of 290; whereas **4** gives the highest TON of 700. On the other hand, complexes **6** and **7**, which have one and no axial pyridine ligand, respectively, do not show any catalytic activity. By using a lower concentration of 2.5 μM, a TON of 1700 could be achieved for **4** (Table S3). The TON was further increased to 2100 in the presence of 1.2% CF₃CH₂OH (instead of CH₃CN).

We then tried to detect any intermediates formed during water oxidation by ESI-MS (Figure S3). The MS of **3** in water (pH 2) exhibits the parent peak [Ru(qpy)(pic)₂]²⁺ (pic = 4-picoline) at m/z = 299. Upon addition of 2 equiv of CAN, an additional peak at m/z = 307 appeared, which may be assigned to [Ru(qpy)(pic)₂+O]²⁺. When another 2 equiv of CAN were added, the parent peak disappeared, and a minor peak at m/z = 315 appeared, which may be assigned to [Ru(qpy)(pic)₂+2O]²⁺. [Ru(qpy)(pic)₂+2O]²⁺ became the predominant peak after addition of 8 equiv of CAN (Figure 4). Similar results were found for **1** and **4**. The observation of peaks with one and two additional O atoms are often assigned as oxo and superoxo/peroxo species, respectively, that is, [Ru(qpy)(pic)₂(O)]²⁺ and [Ru(qpy)(pic)₂(O₂)]²⁺.

We then attempted to isolate these intermediates. Treatment of **3** with excess CAN (40 equiv) in 0.1 M HOTf followed by the addition of NH₄PF₆ resulted in the formation of an orange compound **8**[PF₆]₃ in 50% yield. The X-ray structure of **8**[PF₆]₃ (Figure 5) shows that it consists of the complex [Ru(ONNO)(pic)₂]³⁺ (ONNO = 1,1'-dioxido-2,2':6',2'':6'',2'''-quaterpyridine), in which the ONNO ligand is derived from oxidation of the two outer pyridyl groups of the qpy ligand to a *N,N'*-dioxide. The O1–Ru1–O2 bite angle is 101.86°, which

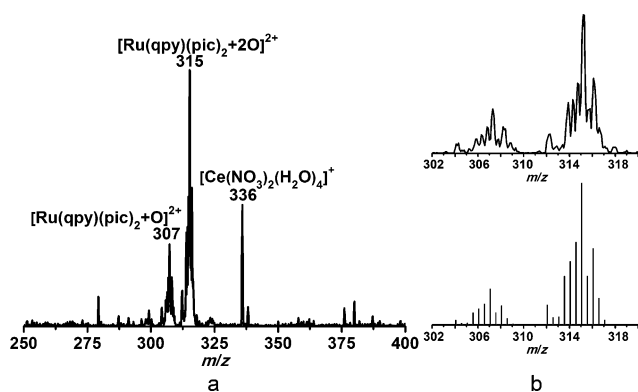


Figure 4. a) ESI-MS of **3** ($[\text{Cl}]_2$ (1.0 mM) in 0.01 M HNO_3 recorded 20 min after the addition of 8 equiv of CAN. The solution was diluted 10 times before electrospraying. b) The expanded (top) and calculated (bottom) isotopic patterns.

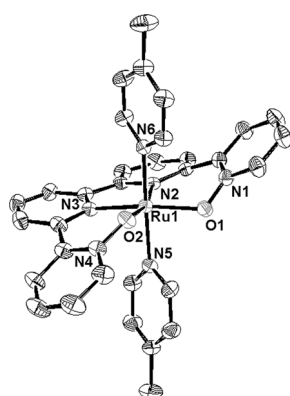


Figure 5. ORTEP plot of **8**. Thermal ellipsoids are drawn at 50% probability; anions, solvent, and hydrogen atoms are omitted for clarity.

is larger than the ideal value of 90° for an octahedral complex, but is much smaller than the N1-Ru1-N4 angle of 120.89° in **3**. The CV of **8** in H_2O (pH 1) shows a reversible $\text{Ru}^{\text{III/II}}$ couple at 0.58 V versus SCE, which is lower than that of its precursor **3** by 0.44 V, in accordance with the replacement of the qpy ligand in **3** by the less π -accepting ONNO ligand in **8**. In contrast to **3**, there is a catalytic current for **8** in CV with an onset potential at around 1.3 V versus SCE (Figure 6). When oxidation of **3** was carried out using 10 equiv instead of 40 equiv of CAN, the CV of the resulting complex **8** contains a minor peak at 0.78 V, which is most likely due to the first oxidation product $[\text{Ru}(\text{NNNO})(\text{pic})_2]^{3+}$ (Figure S4). Based on these results, the $[\text{Ru}(\text{qpy})(\text{pic})_2+\text{O}]^{2+}$ and $[\text{Ru}(\text{qpy})(\text{pic})_2+2\text{O}]^{2+}$ peaks in the MS in Figure 4 should arise from $[\text{Ru}(\text{NNNO})(\text{pic})_2]^{3+}$ and $[\text{Ru}(\text{ONNO})(\text{pic})_2]^{3+}$, respectively, and not from any $\text{Ru}(\text{O})$ or $\text{Ru}(\text{O}_2)$ species.

The isolation of the Ru-ONNO complex **8** raises the interesting question of whether it is a WOC or merely a byproduct. To answer this question, catalytic water oxidation by **8** was studied and compared with the reaction catalyzed by **3**. Oxygen evolution was continuously monitored using an Ocean Optics oxygen sensor (Figure 7). For **8**, O_2 evolution occurred within 1 min after the addition of CAN,

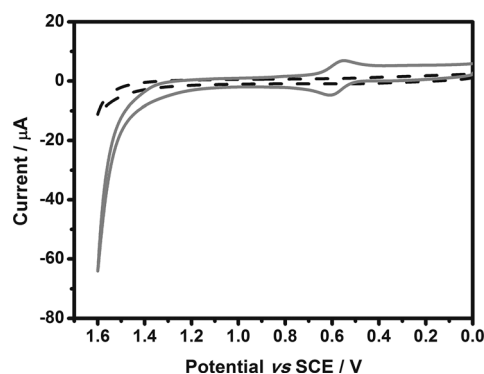


Figure 6. CV of **8** (0.5 mM, solid line) and blank (dashed line) in 0.1 M HOTf. Scan rate = 100 mVs^{-1} .

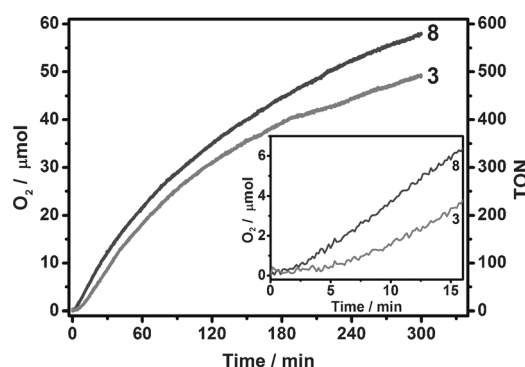


Figure 7. Plots of oxygen evolved and TONs versus time by $20 \mu\text{M}$ of **3** and **8** in 0.1 M HOTf (4.8 mL) and CH_3CN (0.2 mL) containing CAN (200 mM) at 25°C . Inset shows oxygen evolution curves in the first 15 min.

whereas for **3** an induction period of about 5 min was observed under the same reaction conditions. After the induction period, the rate of O_2 evolution by **3** was comparable to that of **8**. The observed induction period for **3** may be interpreted as arising from its initial oxidation to the N,N'' -dioxide complex **8**, which is the real catalyst for water oxidation. This notion is also supported by the observation that **8**, but not **3**, shows a catalytic current in CV.

If complex **8** is the real catalyst, then there is the issue of whether the O atoms in O_2 come from the ONNO ligand, that is, $\text{ONNO} \rightarrow \text{NNNN} + \text{O}_2$, or directly from H_2O , and to answer this question we performed ^{18}O -labeling experiments. We first prepared ^{18}O -labeled **8**, $[\text{Ru}(^{18}\text{ONN}^{18}\text{O})(\text{pic})_2]^{3+}$, by reacting **3** with CAN in H_2^{18}O . A single turnover experiment was then performed by treating ^{18}O -**8** with 4 equiv of CAN in H_2^{16}O under argon in 0.1 M HOTf. The O_2 generated ($0.69 \mu\text{mol}$, yield 58%) was found to be exclusively $^{16}\text{O}^{16}\text{O}$, as analyzed by GC-MS (Figure S5). This means that all O atoms in O_2 came directly from water. Moreover, the ESI-MS of the solution after water oxidation shows only ^{18}O -containing ruthenium species, the predominant peak is $[\text{Ru}(^{18}\text{ONN}^{18}\text{O})(\text{pic})_2]^{2+}$ ($m/z = 317$). A similar mass spectrum was obtained using 16 equiv of CAN (Figure 8). The ESI-MS results again show that the O atoms in O_2 did not come from the ONNO ligand.

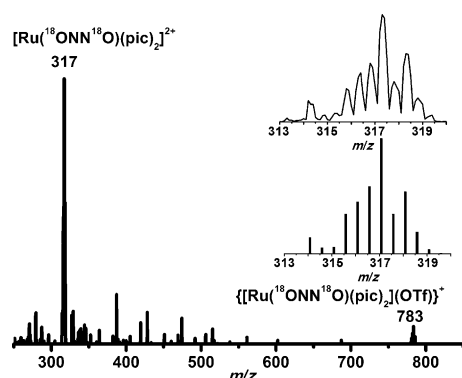


Figure 8. ESI-MS of ^{18}O -labeled **8** after reacting with 16 equiv of CAN in 0.1 M HOTf. Insets show the expanded (top) and calculated (bottom) isotopic patterns.

It also reveals that **8** does not exchange its O atoms with H_2O during the catalysis.

Kinetic studies for water oxidation by **8**/CAN were performed by monitoring the amount of evolved O_2 as a function of time (Figure S6). The initial rate shows a linear dependence on **[8]**, and a first-order rate constant of 2.1 min^{-1} (25°C) was obtained from the slope. This result suggests that catalytic water oxidation by **8** probably occurs through a “water nucleophilic attack” mechanism.^[6b,9a] We propose that the active intermediate is a seven-coordinate ruthenium(V) oxo species, $[\text{Ru}(\text{O})(\text{ONNO})(\text{L})_2]^{2+}$, by analogy to the WOC $[\text{Ru}(\text{bda})(\text{L})_2]^{[8c]}$. DFT calculations have been performed, which indicate that the seven-coordinate ruthenium(V) oxo species is stable with a $\text{Ru}=\text{O}$ distance of $1.767 \text{ \AA}$ (Figure S7).

Polypyridyl ligands are widely used in WOCs and it is generally believed that these ligands are reasonably oxidation-resistant. We have demonstrated that ruthenium(II) complexes bearing a quaterpyridine ligand function only as precatalysts for water oxidation. In the presence of CAN these complexes are readily oxidized to the qpy- N,N'' -dioxide complexes $[\text{Ru}(\text{ONNO})(\text{L})_2]^{3+}$, which are the real WOCs.

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