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Catalytic Water-Oxidation Activity of a Weakly Coupled Binuclear Ruthenium Polypyridyl Complex

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Abstract: The catalytic oxidation of water by the binuclear complex $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)](PF_6)_4$ (tpy_2ph = 1,3-bis(4'-2,2':6',2''terpyridin-4-yl)benzene) was investigated comparatively to its mononuclear counterpart $[Ru(H_2O)(bpy)(phtpy)](PF_6)_2$ (phtpy = 4'phenyl-2,2':6',2"-terpyridine). These catalysts were prepared from the synthesis of their precursor chloride complexes, which were also extensively characterized in this work. The H₂O-Ru(II) complexes undergo proton-coupled electron-transfer processes to generate the redox species HO-Ru(III), O=Ru(IV) and O=Ru(V). The catalytically active species [Ru^V₂(O)₂(bpy)₂(tpy₂ph)]⁶⁺ and [Ru^V(O)(bpy)(phtpy)]³⁺ were generated electrochemically as well as by using cerium(IV) ammonium nitrate. In the presence of Ce(IV), the catalytic rates for O₂ production by the binuclear and mononuclear species were 1.9×10⁻³ s⁻¹ and 9.5×10⁻⁵ s⁻¹, respectively. This superior catalytic performance by the binuclear complex suggests that, despite the weak electronic coupling between Ru centers, the second site can play an important mechanistic role in the formation of the activated species [(bpy)(OO)Ru^{IV}(tpy₂ph)Ru^{III}(OH)(bpy)]⁴⁺.

Introduction

The development of renewable and clean energy sources,^[1] independent of fossil fuels,^[1e, 2] has been needed for the continued development of our society. In this context, H₂ production finds application in the direct use of H₂ as a fuel due to its high energy content^[3] as well as in the production of hydrocarbon fuels from CO₂. Water splitting by the so-called photosynthesis provides a sustainable artificial and environmentally friendly production of H₂ by the catalyzed reaction: 2 H_2O \rightarrow 2 H_2 + O_2 $^{[4]}$ The oxidation half-reaction $(2 H_2O \rightarrow O_2 + 4H^+ + 4 e^-)$ is responsible for the production of protons and electrons to generate H₂.^[4] The complex multielectron/multi-proton mechanism associated with the O-O bond formation has presented major challenges in the development of efficient water-splitting catalysts.^[4b]

Many attempts to develop electrocatalysts for water oxidation using ruthenium polypyridyl complexes have been carried out since the 1980's.^[4b] The first well-characterized system was the blue dimer, $[(bpy)_2(OH_2)Ru^{III}-O-Ru^{III}(OH_2)(bpy)_2]^{4+}$ (bpy = 2,2'-bipyridine), where two ruthenium

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centers are intimately connected by a μ -oxo bridge.^[4b, 4c, 5] This complex exhibits several oxidation states up to Ru^V=O, the catalytically active species for oxidation of water^[4b, 4c] upon successive proton-coupled electron transfer (PCET) reactions. The groups of Tanaka^[6] and Llobet^[7] extended this approach to other binuclear ruthenium polypyridyl complexes in which the metal centers are close enough to interact with each other and promote O₂ evolution from water.

This idea on the necessity of simultaneous interaction of at least two metal centers to activate the oxidation of water persisted until 2005, when Thummel et al. demonstrated high catalytic activity in mononuclear ruthenium complexes.^[8] Soon afterwards, Meyer et al.^[9] proposed a mechanism to explain such activity by using ceric ammonium nitrate (CAN) as oxidizing agent in highly acidic media. Since then, many groups have contributed to this exciting area. For example, Berlinguette et al. carried out a systematic study describing the effect of electron donor and acceptor substituents on bpy and tpy ligands of $[Ru(L)(bpy)(tpy)]^{n+}$ (L = Cl⁻ or H₂O, n = 1 or 2) on the electrocatalytic activity and stability of these complexes.^[10] In addition, they studied how the induced electronic effects influence the interaction of those complexes with CAN, and the influence of the mineral acid on the activity of this oxidizing agent.^[10-11] Sun et al.^[12] studied the ligand substitution with coordinating groups and demonstrated that the presence of electron donors decreases the oxidation potentials while maintaining relatively high electrocatalytic activity for oxidation of water.

Several other water-oxidation mononuclear catalysts have been reported, but the necessity or not of a binuclear active site cannot be completely ruled out because the reaction mechanism of such catalysts seems to involve the interaction of two molecules of the mononuclear complex to generate the activated state. Furthermore, the role of a strong electronic coupling^[4b, 6, 13] observed in the blue dimer and other dimeric catalysts is not clear, despite some theoretical studies in this direction.^[13] Following our interest in this problem, here we report on the synthesis, characterization, and catalytic properties of the binuclear complex $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)](PF_6)_4$, where the two metal centers are almost electronically independent of each other, as demonstrated here by comparison with the related mononuclear complex $[Ru(H_2O)(bpy)(phtpy)](PF_6)_2$ (phtpy = 4'phenyl-2,2':6',2"-terpyridine). Surprisingly, this weakly coupled binuclear complex presented an activity for oxidation of water with a $k_{cat}(O_2)$ about 20 times that of the mononuclear complex, demonstrating a significant cooperation by the second Ru site.

Results and Discussion

Synthesis and Characterization

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The phtpy and tpy₂ph ligands were prepared by the condensation reaction of 2-acetylpyridine with benzaldehyde or isophthalaldehyde in the presence of an ammonia source,^[14] and characterized by ¹H NMR spectroscopy (Fig. S1 and S2), mass spectrometry (ESI-MS) and elemental analysis. The ruthenium aquo complexes were prepared in three steps. First, the tridentate ligands were reacted with RuCl₃·H₂O to obtain the respective trichloro complexes. Then, the [RuCl₃(phtpy)] and [Ru₂Cl₆(tpy₂ph)] precursors were reacted with bpy in the presence of the reducing agent 4-ethylmorpholine to obtain the respective chloro complexes [RuCl(bpy)(phtpy)](PF₆) and $[Ru_2Cl_2(bpy)_2(tpy_2ph)](PF_6)_2.$ In addition to structural characterization by ESI-MS and elemental analysis, the presence of the CI ligand was confirmed by the signal of the H₆" in the NMR spectra (Fig. S3 and S4) at 10.11 and 10.13 ppm for the mono- and binuclear complexes, respectively.^[10a] Finally, the mono- and binuclear aquo complexes [Ru(H₂O)(bpy)(phtpy)](PF₆)₂ and [Ru₂(H₂O)₂(bpy)₂(tpy₂ph)](PF₆)₄ were prepared by facilitated substitution of Cl⁻ by H₂O in the presence of AgNO₃ or CF₃SO₃H, which was confirmed by the shift of the H6" signal to 9.65 and 9.54 ppm, respectively, in the NMR spectra of the mono- and binuclear complexes (Fig. S5 and S6).^[10a]



i) RuCl₃, EtOH, reflux. ii) a) bpy, LiCl, 4-Ethylmorpholine, EtOH:H₂O (3:1), b) NH₄PF₆(aq). iii) AgNO₃, acetone:H₂O (3:1) reflux, or CF₃SO₃H, 1,2-Dichlorobenzene, reflux. **Scheme 1.** Synthetic routes for preparation of the mono- and binuclear aquo complexes [Ru(H₂O)(bpy)(phtpy)](PF₆)₂ and [Ru₂(H₂O)₂(bpy)₂(tpy₂ph)](PF₆)₄.

The mono- and binuclear chloro and aquo Ru(II) complexes exhibit the typical pseudo-octahedral structure and singlet ground state (low-spin $d\pi^6$), as supported by DFT calculations. The fully optimized structures are shown in Fig. 1, and bond distances and angles are provided in the Supporting Information (Tables S1-S4). In the geometry optimization of the aquo complexes, two solvent water molecules were explicitly included as the first hydration shell around the water ligand. As shown in a previous report on [Ru(H₂O)(bpy)(tpy)]^{2+[15]} this approach significantly improves the characterization of electronic

structure as well as the spectral match between calculated (TD-DFT) and experimental electronic absorptions, which is thus relevant to the spectroscopic results below. For evaluation of the DFT structures, the optimized geometries of $[Ru(Cl)(bpy)(phtpy)]^+$ and $[Ru(H_2O)(bpy)(phtpy)]^{2+} \cdot (2H_2O)$ were compared with the X-ray crystallographic data for the related $[Ru(CI)(bpy)(tpy)](PF_6)^{[16]}$ complexes and [Ru(H₂O)(bpy)(tpy)](ClO₄)₂,^[17] respectively, and shown to be in close agreement (Tables S1 and S3).



Figure 1. DFT structures of (A) $[RuCl(bpy)(phtpy)]^{+}$, (B) $[Ru_2Cl_2(bpy)_2(tpy_2ph)]^{2+}$, (C) $[Ru(H_2O)(bpy)(phtpy)]^{2+}$, and (D) $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)]^{4+}$. Full geometry optimizations were performed at the B3LYP//6-31G*(C,H,N,O,Cl)/SDD(Ru) level. The explicit inclusion of two solvent H₂O molecules (W1 and W2) per H₂O ligand (WL) to give the adducts B and D is discussed in the text. Hydrogen atoms of phtpy and tpy2ph are omitted for clarity (atom colors: Ru = purple, N = blue, O = red, Cl = green, C = dark gray, H = light gray). Selected structural parameters are provided in Tables S1-S4, along with additional views of the molecular structures.

In the complexes shown in Fig. 1, the distortion from octahedral geometry around the metal is due to the restricted bite angle of the tridendate ligand. The calculated N1-Ru-N3 angle for the tridendate phtpy and tpy₂ph ligands (157.6–158.3°) and the N4-Ru-N5 angle for the bidentate bpy ligand (77.4-78.2°) are very similar to those of tpy and bpy in {Ru^{II}(bpy)(tpy)} moieties.^[18] For phtpy and tpy₂ph, the calculated Ru-N distance involving the N1 and N3 atoms trans to each other is 2.10-2.11 Å, whereas that involving the central N2 is much shorter (1.98–1.99 Å) as a result of the constraint by such mer-arranged tridentate ligands.^[19] For bpy, the Ru-N distance is 2.11-2.12 Å for N5 and 2.07-2.09 Å for N4, reflecting a stronger $Ru^{II} \rightarrow bpy \pi$ -backdonation at the N atom *trans* to the donor CI⁻/H₂O ligand. The Ru–CI distance of 2.42 Å and Ru–O_{WL} distance of 2.17 Å are also typical of related chloro and aquo complexes.^[17, 20] The angle between the planes of the adjacent rings of phenyl and middle pyridyl groups is 34.6-37.4° for the mononuclear complexes (phtpy) and 42.8-43.1° for the dinuclear complexes (tpy₂ph). The two solvent water molecules (W1 and W2) form H bonds with the Ru-bound water ligand (WL), with O_{WL} ... O_{Wsolv} and $(O_{WL})H$... O_{Wsolv} distances of 2.74 Å and 1.75 Å, respectively (Tables S3 and S4).

Electronic Spectroscopy

The electronic absorption spectra of all mono- and binuclear species (Fig. 2) exhibit a similar pattern, with polypyridyl ligand localized $p\pi \rightarrow p\pi^*$ and $n \rightarrow p\pi^*$ transitions below 350 nm, and Ru($d\pi$) $\rightarrow p\pi^*$ metal-to-ligand charge-transfer (MLCT) transitions above 350 nm. These electronic transitions were assigned in detail with the support of TD-DFT calculations (Fig. S7-S12 and Table S5-S12) by using a well-established approach that has been successfully applied to structurally related complexes of the type [Ru(L)(bpy)(tpy)]ⁿ⁺ (L = Cl⁻ or H₂O, n = 0 or 1).^[15, 21]



Figure 2. Experimental (blue line) and calculated (red line) UV-Vis absorption spectra. Vertical bars (in red) indicate discrete electronic transitions. The spectra of (A) [RuCl(bpy)(phtpy)](PF₆) and (B) [Ru₂Cl₂(bpy)₂(tpy₂ph)](PF₆)₂ were obtained in acetonitrile solution, and the spectra of (C) [Ru(H₂O)(bpy)(phtpy)](PF₆)₂ and (D) [Ru₂(H₂O)₂(bpy)₂(tpy₂ph)](PF₆)₄ were obtained in water. The TD-DFT electronic excitations were calculated at the B3LYP//6-31G^{*}(C,H,N,O,Cl)/SDD(Ru) level.

As listed in Table S5, the three highest occupied molecular orbitals (HOMOs) of the mononuclear $[RuCl(bpy)(phtpy)]^+$ complex are mainly from Ru(II) t_{2g} orbitals with minor

contributions from Cl⁻, phtpy and bpy $p\pi$ orbitals. The two lowest unoccupied molecular orbitals (LUMOs) are nearly degenerate, with one largely dominated by bpy p π * and the other by phtpy p

transitions of both phtpy and bpy ligands.

 π *. The most intense band at 518 nm was assigned to Ru(d π)

 \rightarrow p π *_{bpy+phtpy} (transition #7), for which the natural transition

orbital (NTO) pairs is shown in Fig. S8. The weak, broad

absorption between 350 and 400 nm is associated with multiple

MLCT transitions involving low-lying bpy and phtpy π^* orbitals.

In the UV region, the band at 321 nm is assigned to phtpy p $\pi \rightarrow$

 $p \pi^*$ transitions and the band at 288 nm to internal $p \pi \rightarrow p \pi^*$

viewed as two [RuCl(bpy)(phtpy)]⁺ complexes connected by a

phenyl bridge, and thus displays a similar electronic structure

with only small perturbation. Not surprisingly, the main Vis band

at 522 nm associated with the Ru($d\pi$) \rightarrow $p\pi^*_{\text{bpy+phtpy}}$ transition

The binuclear [Ru₂Cl₂(bpy)₂(tpy₂ph)]²⁺ species can be

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mononuclear species. The MLCT and internal ligand transitions associated with the bands below 400 nm also seem to be only weakly perturbed. The assignment of these bands is analogous to the mononuclear complex, as supported by the TD-DFT calculations (Tables S7 and S8).

As expected, the substitution of Cl⁻ by H₂O perturbed the electronic structure of these complexes, causing an increase in the energy difference between the HOMO and LUMO orbitals (see Fig. S10 and S12). In the mono- and binuclear aquo complexes $[Ru(H_2O)(bpy)(phtpy)]^{2+}$ and $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)]^{4+}$, the main MLCT band in the Vis region is blue shifted to 485 nm and 495 nm, respectively, and assigned in detail as shown in Fig. 3 and S11.



Figure 3. Natural transition orbital (NTO) pairs for the main transition in the visible region for $[Ru_2Cl_2(bpy)_2(tpy_2ph)]^{2+}$ (left) and $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)]^{4+}$ (right).

Electrochemistry and Spectroelectrochemistry

Ruthenium polypyridyl complexes generally exhibit a rich electrochemistry due to accessible redox states associated with metal center and ligands. The presence of two polypyridyl ligands increases the complexity in identifying which one, bpy or phtpy/tpy₂ph, is involved in each reduction process. Typical cyclic voltammograms of the complexes in DMF (chloro species) and aqueous solution at pH 1.0 (aquo species) are shown in Fig. 4, and redox potentials are listed in Table 1.

Table 1. Redox potentials ($E_{1/2}$ vs. NHE) of mono- and binuclear complexes.				
Ru ^{III/IV [d]}	Ru ^{IV/V [e]}	bpy ^{0/-}	phtpy ^{0/-} , tpy ₂ ph ^{0/-}	bpy ^{-/2-}
-		-1.25	-1.43	-
-		-1.24	-1.41	-1.64
+1.07	+1.75	-		
+1.09 ^[f]	+1.75 ^[f]	-		
	no- and binuc Ru ^{III/IV [d]} - - +1.07 +1.09 ^[f]	no- and binuclear complexes Ru ^{III/IV [d]} Ru ^{IV/V [e]} - +1.07 +1.75 +1.09 ^[f] +1.75 ^[f]	no- and binuclear complexes. Ru ^{III/IV} [d] Ru ^{IV/V} [e] bpy ^{0/-} - -1.25 - -1.24 +1.07 +1.75 +1.09 ^[f] +1.75 ^[f]	no- and binuclear complexes. Ru ^{III/IV} [d] Ru ^{IV/V} [e] bpy ^{0/-} phtpy ^{0/-} , tpy ₂ ph ^{0/-} - -1.25 -1.43 - -1.24 -1.41 +1.07 +1.75 - +1.09 ^[f] +1.75 ^[f] -

[a] in DMF; [b] in water at pH 1.0; [c] Ru^{II} -OH₂/ Ru^{III} -OH₂ couple; [d] Ru^{III} -OH₂/ Ru^{IV} =O couple; [e] Ru^{IV} =O/ Ru^{V} =O couple; [f] same redox potential for both Ru centers.

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Figure 4. (A) Cyclic voltammograms of the mononuclear $[RuCl(bpy)(phtpy)](PF_6)$ (black line, $v = 100 \text{ mV s}^{-1}$) and binuclear $[Ru_2Cl_2(bpy)_2(tpy_2ph)](PF_6)_2$ (blue line, $v = 50 \text{ mV s}^{-1}$) complexes in DMF, 0.10 М TBACIO₄. (B) Cyclic voltammograms of the mononuclear $[Ru(H_2O)(bpy)(phtpy)](PF_6)_2$ (red line, $v = 10 \text{ mV s}^{-1}$) and binuclear $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)](PF_6)_4$ (magenta line, $v = 10 \text{ mV s}^{-1}$) complexes in aqueous solution at pH 1.0, 0.10 M KNO₃.

The ligand reduction processes are accessible only in DMF solution, as these processes are outside the working range of water. In the aquo complexes, the coordinated water strongly influences the results because of chemical reactions coupled to the redox process. Thus, only the chloro complexes were evaluated in the region of ligand reductions. The mononuclear [RuCl(bpy)(phtpy)]⁺ species exhibited two redox processes at -1.25 and -1.43 V. The first was assigned to the bpy^{0/-} couple, since spectroelectrochemistry (Fig. S13) in this potential region led to the decrease of the band at 288 nm, which is associated with a $p\pi \rightarrow p\pi^{+}$ transition of bpy. Similarly, the redox process at -1.43 V was assigned to the phtpy^{0/-} couple due to the decrease of the band at 321 nm after reduction of the complex under a potential of -1.6 V (Fig. S13).

Three redox processes at -1.24, -1.41 and -1.64 V were found for the $[Ru_2Cl_2(bpy)_2(tpy_2ph)]^{2+}$ species. The first was assigned to the $bpy^{0'-}$ couple on both moieties, as it led to the decrease of the bpy $p\pi \rightarrow p\pi^*$ transitions at 288 and 321 nm as well as the MLCT band at 522 nm (Fig. S14). The processes at -1.41 and -1.64 V were assigned to the $tpy_2ph^{0'-}$ [22] and both $bpy'^{\prime 2-}$ couples, as confirmed by the spectroelectrochemical changes shown in Fig. S14, particularly the disappearance of the bands at 321 and 295 nm, respectively.



Figure 5. Spectroelectrochemical changes associated with the oxidation of $[RuCl(bpy)(phtpy)](PF_6)$ in DMF (A), $[Ru(H_2O)(bpy)(phtpy)](PF_6)_2$ and $[Ru(OH)(bpy)(phtpy)](PF_6)_2$ in water at pH 7.0 (B, C), $[Ru_2Cl_2(bpy)_2(tpy_2ph)](PF_6)_2$ in DMF (D), and $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)](PF_6)_4$ and $[Ru_2(OH)_2(bpy)_2(tpy_2ph)](PF_6)_4$ in water at pH 7.0 (E, F).

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As for the oxidation processes, the chloro complexes exhibit only one reversible redox process at 0.92-0.94 V assigned to the Ru(III/II) couple,^[13a, 13b, 22] which is spectroelectrochemically supported by the disappearance of the MLCT band at 500-530 nm and the decrease of the ligand $p \pi \rightarrow p \pi^*$ transition around 290 nm (Fig. 5A and 5D). The fact that oxidation occurs on both Ru centers at the same potential (i.e. without separation) clearly show the absence of significant electronic communication between metals, confirming that the redox behavior of Ru centers is independent of each other.

Ligand substitution of Cl⁻ by H₂O shifted that redox process to 0.96-0.98 V and promoted the appearance of a new reversible oxidation at 1.07-1.09 V. Consistent with the above observations for chloro complexes, the behavior of both mono- and binuclear aquo species is very similar and indicates that the electronic coupling between ruthenium sites in the binuclear complex is too weak and insufficient to split their redox potentials. Since each moiety behaves independently, the only difference is that the current intensity of voltammetric waves corresponds to two electrons in the binuclear complex and one electron in the mononuclear species. As detailed below, the redox process at 1.07-1.09 V is assigned to the Ru^{III}-H₂O/Ru^{IV}=O process. Notice that only minor spectroelectrochemical changes was observed for this last process, since the Vis spectral features associated with MLCT vanishes upon the first oxidation to Ru(III).

Proton-Coupled Electron Transfer (PCET) Reactions

The mono and binuclear aquo complexes can undergo PCET and thus are prone to pH-dependent redox reactions. A careful electrochemical study was carried out as a function of pH for the $[Ru(H_2O)(bpy)(phtpy)]^{2+}$ and $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)]^{4+}$ species in order to obtain the Pourbaix diagram shown in Fig. 6.



Figure 6. Pourbaix diagrams for the (A) mononuclear complex $[Ru(H_2O)(bpy)(phtpy)](PF_6)_2$ and (B) binuclear complex $[Ru_2(OH)_2(bpy)_2(tpy_2ph)](PF_6)_4$.

At pH 1, the two reversible processes separated by 110 mV 1.07 V) (E_{1/2}= +0.96and for the mononuclear $[Ru(H_2O)(bpy)(phtpy)]^{2+}$ species (Fig. 4A) were assigned to the 1-electron [Ru^{II}-OH₂]²⁺/[Ru^{III}-OH₂]³⁺ process and 1-electron/2proton [Ru^{III}-OH₂]³⁺/[Ru^{IV}=O]²⁺ process, respectively.^[14c] At such acidic condition (pH 0 to ~1.4), all but the high valence [Ru^{IV}=O]²⁺ species are protonated (Fig. 6A). However, both redox potentials decrease with a linear dependence of about 59 mV/pH as the pH increase from ~1.4 to 10, as described by the [Ru^{II}-OH₂]²⁺/[Ru^{III}-OH]²⁺ PCET reactions and [Ru^Ⅲ-OH]²⁺/[Ru^{IV}=O]²⁺.^[14c]

The UV-Vis absorption spectra of the $[Ru^{II}-OH_2]^{2+}$, $[Ru^{III}-OH]^{2+}$ and $[Ru^{IV}=O]^{2+}$ species as well as spectroelectrochemical changes at pH 7.0 are shown in Fig. 5. When the $[Ru^{II}-OH_2]^{2+}$ complex is oxidized to $[Ru^{III}-OH]^{2+}$, the MLCT band decreases concomitantly with the rise of a new absorption band at 387 nm, characteristic of the OH $(\rho\pi) \rightarrow Ru^{III}(d\pi)$ ligand-to-metal charge transfer (LMCT) transition.^[23] Notice that, in the PCET oxidation of $[Ru^{III}-OH]^{2+}$ to $[Ru^{IV}=O]^{2+}$, this LMCT band disappears and two new bands arise at 334 and 354 nm; the first one was tentatively assigned to the $O^{2-}(\rho\pi) \rightarrow Ru^{IV}(d\pi^*)$ LMCT transition.

At pH < 1.4, the intermediate PCET reaction, whose E_{1/2} shifts with a slope of -118 mV/pH, involves the [Ru^{III}-OH₂]³⁺/[Ru^{IV}=O]²⁺ redox process.^[14c] Finally, the pH-independent [Ru^{IV}=O]²⁺/[Ru^V=O]³⁺ process was observed at 1.7 V (Fig. 6A). This process was revealed by square wave voltammetry and the potentials refer to the anodic peak potentials obtained at each pH (Fig. S15). An analogous behavior was observed for the binuclear species [Ru₂(H₂O)₂(bpy)₂(tpy₂ph)]⁴⁺, except for slight shifts of pKa's and redox potentials in the Pourbaix diagram shown in Fig. 6B.

Catalytic Oxidation of Water

Initially, qualitative evidence for catalytic activity was observed electrochemically. The voltammograms of the mononuclear $[Ru(H_2O)(bpy)(phtpy)](PF_6)_2$ and binuclear $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)](PF_6)_4$ complexes in the expanded 0.0-1.9 V range exhibit the pair of waves typical of the [Rull-OH₂]²⁺/[Ru^{III}-OH₂]³⁺ and [Ru^{III}-OH₂]³⁺/[Ru^{IV}=O]²⁺ redox processes between 0.8 and 1.2 V (Fig. S16). In addition, the anodic wave assigned to the [Ru^{IV}=O]²⁺/[Ru^V=O]³⁺ process is observed around 1.6-1.7 V, at the onset of the exponential increase of the current due to the oxidation of water to dioxygen.[9b, 10b] The [Ru^{IV}=O]²⁺ species is relatively stable and can be easily characterized by spectroscopic or electrochemical methods. In contrast, the $[Ru^{V}=O]^{3+}$ species is transient due to its catalytic activity for oxidation of water to dioxygen.

In order to obtain quantitative confirmation of catalytic water-oxidation activity by these complexes, direct measurement of O₂ production was performed in liquid phase using an oxygen detection system equipped with a Clark-type electrode (see experimental section for detailed method). In these experiments, the chemical oxidant (NH₄)₂[Ce(NO₃)₆] (CAN; 10 mM in 0.1 M HNO₃) was used as oxidizing agent in the Ru-catalyzed reaction: 4 Ce(IV)_(aq) + 2 H₂O_(I) \rightarrow 4 Ce(III)_(aq) + O_{2(g)} + 4 H⁺_(aq). Kinetic curves based on O₂ formation exhibiting the typical saturation profiles for about 4 h of reaction are represented in Fig. 7.



Figure 7. O₂ evolution as a function of reaction time for 1.0 mL aqueous solutions (0.10 HNO₃; pH 1.0) of the Ru complexes in the presence of 10 mM CAN. In the representative curves above, the concentrations of $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)](PF_6)_4$ (blue line) and $[Ru(H_2O)(bpy)(phtpy)](PF_6)_2$ (red line) are 50 μ M and 100 μ M, respectively, to facilitate a direct comparison of catalytic activity per Ru site (i.e. same amount of Ru in both runs).

By varying the concentration of Ru catalysts (Fig. S17), the values of k_{obs} for O₂ evolution were determined by the initial rate method as a linear function of the concentration; i.e. a first-order dependence, with $d[O_2]/dt = k_{obs} = k_{cat}[Ru \text{ complex}]^{[9, 10b]}$ The rate constants (k_{cat}) evaluated from the slope of the k_{obs} vs [Ru complex] plots (Fig. 8) were found to be 1.9×10^{-3} s⁻¹ for s⁻¹ 9.5×10⁻⁵ $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)]^{4+}$ and for $[Ru(H_2O)(bpy)(phtpy)]^{2+}$. These rates correspond to turnover frequencies (TOF) of 0.11 min⁻¹ and 5.7x10⁻³ min⁻¹, indicating that the catalytic activity of the binuclear complex is much higher (by about 20 times) compared to the mononuclear species. Another significant difference is that an induction period of 100-200 s was typically observed for the mononuclear complex (Fig. S17), while the binuclear complex exhibited water-oxidation activity immediately upon mixing with Ce(IV). This observation suggests that an intermediate species formed in situ (possibly involving the association of another Ru site) is the actual active species from the mononuclear complex. These results show that the binuclear complex is a superior catalyst overall.



Figure 8. Plots of initial rates for O₂ evolution (k_{obs}) as a function of catalyst concentration, from which the catalytic rates $k_{cat}(O_2)$ were determined to be $1.9 \times 10^{-3} \text{ s}^{-1}$ for $[\text{Ru}_2(\text{H}_2\text{O})_2(\text{bpy})_2(\text{tpy}_2\text{ph})](\text{PF}_6)_4$ (blue line) and $9.5 \times 10^{-5} \text{ s}^{-1}$ for $[\text{Ru}(\text{H}_2\text{O})(\text{bpy})(\text{phtpy})](\text{PF}_6)_2$ (red line).

The oxidation of water by the mononuclear complex should involve the oxidation of $[Ru^{II}(H_2O)(bpy)(phtpy)]^{2+}$ to the active $[Ru^{V}(O)(bpy)(phtpy)]^{3+}$ by a stepwise mechanism in which two proton-coupled electron transfer processes give the high-valent [Ru^{IV}(O)(bpy)(phtpy)]²⁺ that is further oxidized by one electrontransfer process to the catalytically active species.^[9, 10b, 13c] Then, the O-O bond is formed by water nucleophilic attack (WNA) to the oxo group,^[9, 10b, 13c] generating the intermediate [Ru^{III}(OOH)(bpy)(phtpy)]²⁺ species that is oxidized by a PCET process to $[Ru^{V}(OO)(bpy)(phtpy)]^{2+}$, which releases O_2 and regenerates the starting species upon bonding of a water molecule. This should be the rate-limiting step in the catalytic cvcle. Decomposition occurs by intramolecular electronic redistribution and charge transfer with release of O2.[9, 13c] A similar mechanism leading to the formation of the (OH)Ru^{III}-Ru^{IV}(O-O) species after intramolecular PCET mediated by a water molecule is proposed for binuclear catalysts with weakly interacting sites.[13c]

According to our DFT calculations, the Ru-Ru distance in the binuclear species is 13.9 Å, precluding the interaction of the Ru=O sites and direct coupling to form the O=O bond.^[13a, 13c] Therefore, WNA should be the operating mechanism for this binuclear catalyst, where each site operates independently from another.^[13a, 13c] In this case. WNA one to the [(bpy)(O)Ru^V(tpy₂ph)Ru^{IV}(O)(bpy)]⁵⁺ intermediate generates the [(bpy)(HOO)Ru^{III}(tpy₂ph)Ru^{IV}(O)(bpy)]⁴⁺ species that is converted to the activated complex responsible for O₂ release by a PCET modulated by a water molecule. Thus, the second Ru center plays a key role by effectively acting as an oxidant and nucleophile responsible for converting [Ru^{III}(OOH)]²⁺ into $[Ru^{IV}(OO)]^{2+}$, whereas $[Ru^{IV}(O)]^{2+}$ is reduced to $[Ru^{III}(OH)]^{+}$ in the formation of $[(bpy)(OO)Ru^{IV}(tpy_2ph)Ru^{III}(OH)(bpy)]^{4+}$. The superior performance of the binuclear catalyst compared to the mononuclear confirms that the PCET process mediated by a water molecule is a key and possibly rate-limiting step in the catalytic cycle (as proposed by Van Voorhis) and that the binuclear species has a more suitable structure to generate the (OH)Ru^{III}–Ru^{IV}(O-O) species responsible for the production of O₂.

Conclusions

The structurally related mononuclear $[Ru(H_2O)(bpy)(phtpy)](PF_6)_2$ and binuclear $[Ru_2(H_2O)_2(bpy)_2(tpy_2ph)](PF_6)_4$ complexes were synthesized, characterized, and utilized to comparatively study the performance of water-oxidation catalysts with one *versus* two weakly coupled catalytic sites. Unlike structures designed for close cooperation between active sites, the binuclear complex reported here features Ru centers that are 13.9 Å apart and very weakly coupled electronically. Interestingly, however, the ability of this binuclear catalyst toward water oxidation with relatively

fast O_2 evolution rates (k_{cat}) was found to outperform its mononuclear counterpart by over an order of magnitude. Adding to the complexity in the design and uderstanding of wateroxidation catalysts, these findings suggest that the presence of such remote, weakly interacting Ru sites can be structurally beneficial in some cases, presumably by facilitating the intramolecular PCET leading to the formation of activated species.

Experimental Section

Analytical grade reagents were used without purification in all experiments. HNO₃ stock solutions were prepared with bi-distilled acid. Experiments were performed in 9:1 v/v water/CF3CH2OH solution to increase the solubility of the ruthenium complexes. ¹H NMR spectra were recorded on a Bruker DRX 500 MHz instrument, using suitable solvents and tetramethylsilane (or the solvent peak) as reference. Mass spectra (ESI-MS) were collected using a Bruker Daltonics Esquire 3000 Plus equipment with the capillary potential set to 4 kV and sample injection rate to 180 µL h⁻¹. Elemental analyses were performed using a Perkin Elmer 2400 series II analyzer. UV-Vis absorption spectra were obtained using a Hewlett Packard 8453A diode array spectrophotometer. Cyclic voltammograms were measured using an Autolab PGSTAT30 potentiostat and a conventional three-electrode cell consisting of a platinum (organic solvent) or glassy carbon (aqueous medium) working electrode, a platinum wire as auxiliary electrode, and a reference electrode made of Ag/AgNO3 (10 mM; +0.503 V vs. NHE) or Ag/AgCI (1.0 M KCl; +0.222 V vs. NHE) for organic and aqueous media, respectively. Tetrabutylammonium perchlorate (TBACIO₄; 0.10 M) and KNO3 (0.10 M) were used as electrolyte in organic and aqueous media. A solution of Na₄[Fe(CN)₆] (E_{1/2} = +0.360 V vs NHE) was also used as external reference for calibration of potentials.^[24] Measurements as a function of pH were performed using 5 mL of an aqueous solution of 1 mM complex in 0.10 M KNO3 buffered with 10 mM Britton-Robinson buffer,^[25] the pH was adjusted by controlled addition of microliter volumes of 1.0 or 4.0 M KOH solution. UV-Vis absorption spectroelectrochemistry was carried out using a custom-built electrochemical cell consisting of a gold minigrid working electrode, an Ag/AgNO₃ (10 mM in acetonitrile) or Ag/AgCl (1.0 M KCl; +0.222 V vs. NHE) reference and a platinum wire auxiliary electrode mounted inside a quartz cuvette with a pathlength of 25 μ m. The application of potentials was controlled by an EG&G PAR 173 potentiostat and the spectra were recorded on a HP 8453A spectrophotometer. Oxygen evolution was measured in liquid phase using a Hansatech Instruments, Oxygraph System (OXYG1 and DW1/AD unit) equipped with a Clark-type oxygen electrode (S1 or S1/MOD). The electrode surface was protected from the sample by a freshly installed Teflon membrane. Detection of O₂ was recorded at 1-second intervals using the Oxygraph Plus software. The signal was calibrated using oxygen-free and air-saturated aqueous solutions at a temperature of 20 °C and local atmospheric pressure of 77 kPa. Freshly prepared stock solutions of Ru complexes and CAN in 0.1 M $\ensuremath{\mathsf{HNO}_3}$ were used in the experiments. Solutions of the complexes were diluted to the appropriate concentrations and flushed in the reaction chamber with argon for 15-20 min to completely remove dissolved oxygen (steady baseline readout around 1 nmol mL⁻¹). The gas in the headspace above the solution was expelled using a gas-tight threaded plunger. To start the oxygen evolution reaction, 10 μ L of a fully deoxygenated 1.0 M CAN solution was injected using a high-precision Hamilton syringe through the plunger into 1.0 mL of the Ru sample at various concentrations (20-200 µM). Initial rates of O₂ production were determined for nearly linear regions of the kinetic curves within the first minutes of reaction. During the experiments. the temperature was kept constant at 20 °C. Density functional theory (DFT) calculations were carried out using the Gaussian 09 revision D.01 software.^[26] The hybrid B3LYP^[27] functional with the SDD^[28] relativistic effective core potential and associated basis set for Ru and the 6-31G(d) basis set^[29] for all the other elements were used for geometry optimization without any constraint. Following optimization, vibrational frequencies were computed at the same level of theory to verify the nature of all stationary points as true minima with no imaginary frequencies. The electronic excitation spectra in the UV/Vis region were obtained by time-dependent DFT (TD-DFT)^[30] calculations, which included the first (lowest-energy) 100 transitions using the same level of theory as above for geometry optimization. Natural transition orbitals (NTOs)^[31] were generated to facilitate visualization and interpretation of electronic transitions from TD-DFT calculations.

4'-phenyl-2,2':6',2''-terpyridine (phtpy): Benzaldehyde (1.10 g, 10 mmol) in 50 mL of ethanol) was reacted at room temperature with KOH (1.50 g), 2-acetylpyridine (2.42 g, 20 mmol) and 30 mL of 28% NH₄OH. The precipitate formed after 4 h was filtered off, washed with water and ethanol, and purified by recrystallization in a 7:3 v/v ethanol/water mixture. Yield: 2.0 g (62%). ¹H NMR (chloroform-*d*, 500 MHz) δ (ppm) (m, *J*, H): 8.77 (s, 2H), 8.75 (dd, 4.8 Hz, 2H), 8.70 (d, 7.9 Hz, 2H), 7.93 (d, 7.0 Hz, 2H), 7.91 (t, 7.8 Hz, 2H), 7.53 (dd, 7.4 Hz, 2H), 7.47 (t, 7.3 Hz, 1H), 7.38 (t, 7.7 Hz, 2H). C₂₁H₁₅N₃ (MW = 309.4), CHN exp(calc)%: 80.27(81.53); 4.72(4.89); 13.21(13.58); ESI-MS (m/z) exp(calc) [phtpy-H]⁺: 310.1(310.3).

1,3-bis(4'-2,2':6',2''-terpyridyl)benzene (tpy₂**ph):** A solution of KOH (1.67 g) in polyethylene glycol 300 (35 mL) was transferred to a beaker and cooled in an ice/water bath. Then, 2-acetylpyridine (3.61 g, 29.84 mmol) and *m*-phthalaldehyde (1.0 g, 7.46 mmol) were added and the homogenized mixture was maintained at 0 °C for 2 h. Finally, 25 mL of 28% NH₄OH was added and the reaction mixture kept at 100 °C for additional 2 h. The precipitate formed was filtered off, washed with water and ethanol, and purified by recrystallization in a 7:3 v/v ethanol/water mixture. Yield: 1.6 g (40%). ¹H NMR (chloroform-*d*, 500 MHz) δ (ppm) (m, *J*, H): 8.83 (s, 4H), 8.75 (d, 4.8 Hz, 4H), 8.71 (d, 7.9 Hz, 4H), 8.37 (s, 1H), 7.99 (d, 7.6 Hz, 2H), 7.91 (t, 7.8 Hz, 4H), 7.68 (t, 7.6 Hz, 1H), 7.37 (d, 7.4 Hz, 4H). C₃₆H₂₄N₆·H₂O (MW = 558.6) CHN exp(calc)%: 77.40(76.93), 4.69(4.67), 15.04(15.02); ESI-MS (m/z) [tpy₂ph-H]⁺: 541.1(541.6).

[RuCl₃(phtpy)]: This mononuclear precursor was prepared by refluxing phtpy (0.10 g, 0.32 mmol) and RuCl₃·H₂O (0.080 g, 0.35 mmol) in 50 mL of anhydrous ethanol for 4 h. After cooling to room temperature, the brown solid was filtered off, washed with ethanol, and dried under vacuum. Yield: 0.150 g (90%).

[Ru₂Cl₆(tpy₂ph)]: This binuclear precursor was prepared by refluxing tpy₂ph (0.180 g, 0.33 mmol) and RuCl₃·H₂O (0.150 g, 0.66 mmol) in 50 mL of anhydrous ethanol for 12 h. A brown solid was filtered off, washed with ethanol, and dried under vacuum. Yield: 0.255 g (80%).

[RuCl(bpy)(phtpy)](PF₆): The crude [RuCl₃(phtpy)] complex (0.10 g, 0.02 mmol) was refluxed with bpy (0.031 g, 0.02 mmol), LiCl (0.043 g, 1.0 mmol) and 4-ethylmorpholine (1.0 mL) in 30 mL of a 3:1 v/v ethanol/water mixture. After 4 h, the solution was filtered and concentrated in a flash evaporator under vacuum. Then, the complex was precipitated using an aqueous NH₄(PF₆) solution. The hexafluorophosphate product was filtered off, washed with water, dried in a desiccator under vacuum, and purified by column chromatography using neutral alumina as stationary phase and mixtures of CHCl₃ and CH₃CN with increasing polarity as eluent. Yield: 0.115 g (80%). ¹H NMR (DMSO-*d*₆, 500 MHz) δ (ppm) (m, *J*, H): 10.11 (d, 5.7 Hz, 1H), 9.19 (s, 2H), 8.94 (d, 7.9 Hz, 2H), 8.92 (d, 8.9 Hz, 1H), 8.64 (d, 8.2 Hz, 1H), 8.37 (t, 8.4 Hz, 1H), 8.32 (s, 1H), 8.08 (t, 8.0 Hz, 1H), 8.03 (t, 7.8 Hz, 2H),

 $\begin{array}{l} 7.78 \ (t, 7.9 \ Hz, 1H), 7.72 \ (d, 7.6 \ Hz, 2H), 7,64 \ (d, 4.8 \ Hz, 2H), 7.62 \ (t, 7.6 \ Hz, 1H), 7.42 \ (d, 5.8 \ Hz, 1H), 7.40 \ (dd, 7.4 \ Hz, 2H), 7.08 \ (t, 7.8 \ Hz, 1H). \\ \lambda_{max} \ nm \ (DMF) \ (\epsilon \ (M^{-1} \ cm^{-1})): 518 \ (1.2 \times 10^4), 368 \ (1.0 \times 10^4), 321 \ (2.5 \times 10^4), \\ 288 \ (4.9 \times 10^4). \ C_{31} H_{23} CIF_6 N_5 PRu \ (MW = 747.0) \ CHN \ exp(calc) \ (H) \ 49.55 \ (49.84), \\ 3.52 (3.10), \ 9.06 (9.37). \ ESI-MS \ (m/z) \ exp(calc) \ (Ru(CI)(bpy)(phtpy)]^*: 602.1 \ (602.1). \end{array}$

[Ru₂Cl₂(bpy)₂(tpy₂ph)](PF₆)₂: The crude [Ru₂Cl₆(tpy₂ph)] complex (0.10 g; 0.10 mmol) was refluxed with bpy (0.032 g; 0.20 mmol), LiCl (0.042 g; 10 mmol) and 4-ethylmorpholine (1mL) in 50 mL of a 3:1 v/v ethanol/water mixture for 8 h, under N2 atmosphere. The volume of the reaction mixture was reduced to about 10 mL in a flash evaporator and the complex was precipitated with an aqueous NH₄PF₆ solution. The solid product was filtered off, washed with cold deionized water, dried in a desiccator under vacuum, and purified by column chromatography using neutral alumina as stationary phase and mixtures of CHCl_{3} and CH₃CN with increasing polarity as eluent. Yield: 0.060 g (40%). ¹H NMR (DMSO-d₆, 500 MHz) δ (ppm) (m, J, H): 10.13 (d, 5.4 Hz, 2H), 9.38 (s, 4H), 9.07 (s, 1H), 9.01 (d, 8.1 Hz, 4H), 8.95 (d, 8.1 Hz, 2H), 8.68 (d, 8.2 Hz, 2H), 8.52 (d, 8.1 Hz, 2H), 8.39 (t, 8.0 Hz, 2H), 8.10 (t, 6.5 Hz, 2H), 8.07 (t, 1H), 8.06 (t, 7.3 Hz, 4H), 7.82 (t, 7.7 Hz, 2H), 7.67 (d, 5.5 Hz, 2H), 7.47 (d, 5.8 Hz, 2H), 7.43 (t, 6.7 Hz, 4H), 7.13 (t, 6.7 Hz, 2H). $\lambda_{max} \ nm$ (DMF) (ɛ (M⁻¹ cm⁻¹)): 522 (2.1×10⁴), 354 (1.9×10⁴), 321 (4.6×10⁴), 293 (9.1×10^{4}) . $C_{56}H_{40}Cl_2F_{12}N_{10}P_2Ru_2 \cdot 3H_2O$ (MW = 1470.0) CHN exp(calc)%: 45.49(45.75), 3.66(3.15), 8.54(9.53). ESI-MS (m/z) exp(calc) [Ru₂Cl₂(bpy)₂(tpy₂ph)]²⁺: 563.0(563.0)

[Ru(H2O)(bpy)(phtpy)](PF6)2: This aquo complex was prepared by reacting [RuCl(bpy)(phtpy)](PF₆) (0.10 g, 0.13 mmol) with AgNO₃ (0.022 g, 0.13 mmol) in 30 mL of a 3:1 v/v acetone/water mixture at 60 °C. The mixture was filtered through a celite bed to remove the AgCI precipitate and the filtrate was concentrated in a flash evaporator. The product precipitated with a NH₄(PF₆) solution was washed with cold water and dried in a desiccator under vacuum. Yield: 0.105 g (90%). ¹H NMR (D₂O: acetone- d_6 (7:3), 500 MHz) δ (ppm) (m, J, H): 9.65 (d, 5.8, 1H), 8.97 (s, 2H), 8.80 (d, 8.5, 1H) 8.72 (d, 8.55 Hz, 2H), 8.47 (d, 8.8 Hz, 1H), 8.42 (t, 9.4 Hz, 1H), 8.17 (d, 7.63 Hz, 2H), 8.13 (t, J= 8.1 Hz, 1H), 8.05 (t, J= 9.50 Hz, 2H), 7.90 (d, J= 5.76 Hz, 2H), 7.78 (t, J= 8.4 Hz, 1H), 7.75 (t, J= 8.2 Hz, 2H), 7.67 (t, J= 8.7 Hz, 1H), 7.49 (d, J= 6.1 Hz, 1H), 7.45 (t, J= 7.40 Hz, 2H), 7.05 (t, J= 8.7 Hz, 1H). λ_{max} nm (H₂O, pH 3.0) (ε (M⁻¹ cm⁻¹ 485 $(1.3 \times 10^4),$ 315 $(3.6 \times 10^4),$ 284 (6.4×10^4) . $C_{31}H_{25}F_{12}N_5OP_2Ru \cdot 2H_2O$ (MW = 910.6) CHN exp(calc)%: 49.55(49.84), 3.52(3.10), 9.06(9.37). ESI-MS (m/z) exp(calc) [Ru(H₂O)(bpy)(phtpy)]²⁺: 292.5 (292.3)

[Ru₂(H₂O)₂(bpy)₂(tpy₂ph)](PF₆)₄: The [Ru₂Cl₂(bpy)₂(tpy₂ph)](PF₆)₂ complex (0.10 g) was refluxed with 5 mL of CF_3SO_3H in 10 mL of odichlorobenzene under N₂ atmosphere for 2 h. The mixture was cooled in an ice/water bath; then, the product was precipitated and washed with diethyl ether and dried in a desiccator. The solid was dissolved in 10 mL of a 3:1 v/v methanol/water mixture, precipitated with a NH₄(PF₆) solution, washed with cold water, and dried in a desiccator under vacuum. Yield: 0.085 g (70%). ¹H NMR (D₂O: acetone-d₆ (7:3), 500 MHz): 9.54 (d, 6.0 Hz, 2H), 9.03 (s, 4H), 8.77 (s, 1H), 8.69 (d, 8.8 Hz, 2H), 8.66 (d, 8,7 Hz, 4H), 8.37 (d, 8.8 Hz, 2H), 8.31 (t, 8.1 Hz, 2H), 8.29 (d, 2H), 8.03 (t, 7.2 Hz, 2H), 7.96 (t, 8.1 Hz, 4H), 7.94 (t, 1H), 7.80 (d, 5.9 Hz, 4H), 7.67 (t, 8.2 Hz, 2H), 7.34 (t, 7.1 Hz, 4H), 7.28 (d, 6.3 Hz, 2H), 6.87 (t, 7.2 Hz, 2H). λ_{max} nm (H₂O, pH 3.0) (ϵ (M⁻¹ cm⁻¹)): 491 (2.7×10⁴), 314 (7.4×10⁴), 287 (13.2×10^4) . $C_{56}H_{44}Cl_2F_{24}N_{10}O_2P_4Ru_2\cdot 3H_2O$ (MW = 1725.1) CHN exp(calc)%: 38.96(38.99), 2.77(2.92), 7.82(8.12).

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FULL PAPER



Water oxidation, Ruthenium polypyridyl, Electronic coupling

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Catalytic Water-Oxidation Activity of a Weakly Coupled Binuclear Ruthenium Polypyridyl Complex

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Weakly coupled binuclear complex shows up to twenty times larger rate constant for oxygen evolution as compared with the analogous mononuclear complex, indicating a major role of the second site on the catalytic activity.