

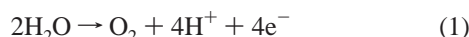
A New Ru Complex Capable of Catalytically Oxidizing Water to Molecular Dioxygen

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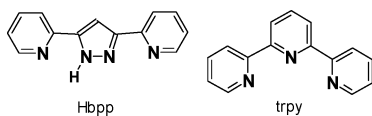
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Oxidation of water to molecular dioxygen is the terminal reaction of green plants, photosystem II (PSII).¹



It is a thermodynamically demanding reaction, since $E^\circ = 1.23$ V at pH = 1.0. On the other hand, it is of tremendous molecular complexity from a mechanistic perspective, since it involves the oxidation of water by 4H^+ and 4e^- with concomitant formation of an oxygen–oxygen bond.² This is an important reaction to be modeled since efficient models can be a first step toward creating a clean, renewable energy source.³ Recently, substantial efforts have been directed at the elucidation of the structure and water oxidation mechanisms that take place at the oxygen-evolving complex (OEC) of PSII.^{4,5} EXAFS studies have disclosed the presence of a Mn tetramer that contains two linked di- μ -oxo dimeric units.^{4,6} There are very few well-defined molecules that are capable of oxidizing water to molecular dioxygen in the homogeneous phase and in the absence of light, as it happens in the PSII–OEC.⁷ Only two manganese complexes have been shown capable of doing so⁸ that can be considered an OEC model; a number of Ru complexes containing the Ru–O–Ru motif have this ability, a paradigmatic example being the blue dimer *cis,cis*-[Ru(bpy)₂(H₂O)]₂O(ClO₄)₄, **4** (bpy = 2,2'-bipyridine).⁹ However, in both cases, in the homogeneous phase the turnover numbers are low.

In the present Communication, we present the first example of a well-characterized (from structural and electrochemical viewpoints) dinuclear Ru complex capable of oxidizing water to O₂ that does not contain the Ru–O–Ru motif. Instead, two Ru metals have been deliberately placed in close proximity and in an adequate orientation using the dinucleating Hbpp and the meridional trpy ligands shown below.



The reaction of [RuCl₃(trpy)] with the dinucleating ligand bpp[−] (deprotonated upon addition of NaMeO; see Supporting Information for synthetic details) in the presence of NEt₃ and LiCl generates the μ -chloro dinuclear ruthenium complex [Ru₂^{II}(μ -Cl)(bpp)(trpy)₂](PF₆)₂, **1**. The μ -chloro bridge is then simply replaced by a μ -acetato bridge, generating [Ru₂^{II}(μ -OAc)(bpp)(trpy)₂](PF₆)₂, **2**, in good yield.¹⁰

The crystal structures of **1** and **2**·2MeCOMe have been solved by X-ray diffraction analysis, and their cationic moieties are dis-

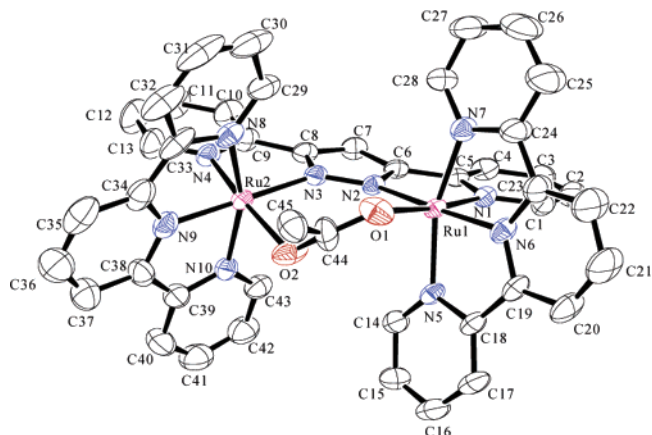
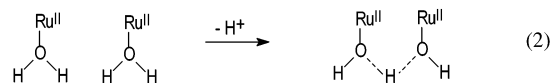


Figure 1. ORTEP plot (ellipsoids at 40% probability) X-ray structure of the cationic moiety of [Ru₂^{II}(μ -OAc)(bpp)(trpy)₂]²⁺, **2**, together with labeling scheme.

played as Supporting Information (together with CIF files) and in Figure 1, respectively.

In complex **2**, it is interesting to observe the distortion imposed by the bridging acetato ligand, producing an elongation of 4.3 pm in the Ru–Ru distance with regard to complex **1** and also an inverse relative rotation of the terpyridyl groups with regard to the central pyrazolylic one of bpp[−] that induces an angle of 12.4° between the bpp[−] pyridylic rings.

Under acidic conditions, the acetato bridge of **2** is replaced by aqua ligands, generating [Ru₂^{II}(bpp)(trpy)₂(H₂O)₂]³⁺, **3**, that has been characterized in solution through spectroscopic and electrochemical techniques (NMR spectra for complexes **1**–**3** and their assignment are shown in the Supporting Information). We have not been able to isolate it in the solid state due to its high solubility in water and in polar organic solvents. Spectrophotometric titration of **3** yields a pK_a of 6.70, which is 4.39 log units lower than that for the related mononuclear complex *out*-[Ru^{II}(Hbpp)(trpy)(H₂O)]²⁺.¹¹ This increase in acidity is tentatively attributed to the formation of the highly stable {Ru₂O₂H₃} entity



that is favored by the intrinsic geometry of the dinucleating ligand, thus manifesting a genuine cooperative effect between metal centers, strategically situated in close proximity thanks to the bpp[−] ligand.

Ru–aqua polypyridyl complexes have rich redox properties since different oxidation states with different degrees of protonation are accessible within a narrow potential range.¹² This is also the case for complex **3**, as exemplified by its corresponding Pourbaix diagram displayed in Figure 2.

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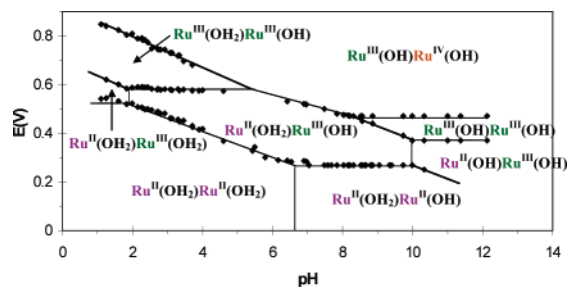
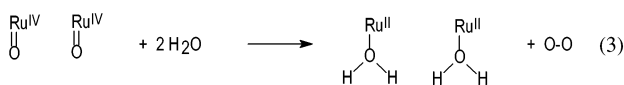


Figure 2. $E_{1/2}$ vs pH or Pourbaix diagram of **3**. The pH–potential regions of stability for the various oxidation states and their dominant proton compositions are indicated. The pK_a values are shown by the vertical solid lines in the various E –pH regions.

For instance, at $\text{pH} = 1.0$, three chemically reversible redox processes are observed, reaching the oxidation state $\text{Ru}^{\text{IV}}\text{Ru}^{\text{III}}$.¹⁰ A fourth, chemically irreversible wave is also observed at $E_{\text{p,a}} = 1.05$ V, which is presumably due to the formation of the $\text{Ru}^{\text{IV}}(\text{O})\text{Ru}^{\text{IV}}(\text{O})$ complex. The chemical irreversibility of this wave is associated with the formation of molecular dioxygen, a point that was verified in a bulk experiment.



The redox properties of **3** are radically different from those of the blue dimer **4**, as can be seen in the Pourbaix diagram, due mainly to the absence of the Ru–O–Ru group. In the latter, the highest oxidation state that can be reached is the V,V, which is in turn responsible for the oxo–oxo coupling that finally leads to the formation of molecular oxygen and thus triggers the oxidation of water; in **3**, the highest oxidation state is IV,IV, which is also responsible for triggering the water-splitting process. On the other hand, for **3**, both II,II and II,III oxidation states are stable, whereas for the blue dimer, oxidation states lower than III,III cause the cleavage of the oxo bridge.

The system 0.914 mM **3**/93.0 mM Ce^{IV} in 0.1 M triflic acid up to a total volume of 2 mL generates molecular oxygen very fast, giving an overall yield of 34 μmol of molecular oxygen (18.6 metal cycles) after 48 h with an efficiency of 73.0% with regard to the oxidant (see Supporting Information for a graph of O_2 evolution vs time). Initially the $\text{Ce}(\text{IV})$ is used to oxidize **3** to its $\text{Ru}^{\text{IV}}\text{Ru}^{\text{IV}}$ oxidation state very fast,¹³ followed by a slower pseudo-first-order process involving the coupling of the oxo groups to form molecular oxygen, with a rate constant of $1.4 \times 10^{-2} \text{ s}^{-1}$.

It is interesting to compare the rate of **3** with that of **4**; the rate is more than 3 times slower for the latter under similar conditions ($4.2 \times 10^{-3} \text{ s}^{-1}$).¹⁴ This substantial increase in activity can be attributed to (a) a more favorable disposition of the Ru=O groups in **3** that are rigidly facing each other, whereas in **4** the rotation along the Ru–O–Ru bonds can slow the process; (b) the fact that complex **3** also benefits from the absence of the oxo bridge when compared to the blue dimer **4**, thus avoiding decomposition by reductive cleavage and by the strong thermodynamic driving force to *trans*-dioxo formation;¹⁵ and (c) the competing anation side reaction that deactivates the complex in **4**,² which takes place to a lower degree in **3**, since the overall charge of the active complex, as well as the Ru oxidation states, are lower.

The water-splitting rate presented by **3** constitutes one of the highest initial rates reported to date, although it is about 4 times slower than that of $[(\text{NH}_3)_3\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{NH}_3)_3]^{2+}$ ($5.6 \times 10^{-2} \text{ s}^{-1}$) reported by Kaneko.¹⁶ However, the latter system suffers from deactivation processes that generate N_2 , that in turn are responsible

for a very narrow range of linear behavior. In sharp contrast, complex **3**, as shown in the inset of Figure S7 (Supporting Information), has a range of linearity that is more than an order of magnitude higher than that of $[(\text{NH}_3)_3\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{NH}_3)_3]^{2+}$. Thus, complex **3** constitutes the most rugged system capable of oxidizing water to molecular oxygen reported to date.

Mechanistically, complex **3** is also highly interesting since, due to the *in, in* configuration of the oxo ligands and the strategic disposition and encumbrance of the trpy ligands, intermolecular oxo–oxo interaction should be negligible and therefore only the intramolecular pathway for dioxygen formation can operate in this complex.

Even though the overall performance of **3** is remarkably superior to that of **4**, deactivation pathways presumably caused by ligand oxidation due to intermolecular interactions still do operate, limiting the number of turnovers obtained. We are now in the process of elucidating and understanding such pathways in order to be able to design more robust and effective systems as well as designing their heterogenized analogues.

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Supporting Information Available: CIF files together with additional structural, spectroscopic, and electrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>. Supplementary crystallographic data for this paper (CCDC 237038 for **1** and 237037 for **2**) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Rd., Cambridge CB2 1EZ, U.K.; fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

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