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Quantum Chemical Study of the Mechanism of Water Oxidation Catalyzed by a Heterotrinnuclear Ru₂Mn Complex

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Abstract

The heterotrinnuclear complex **A** $\{[\text{Ru}^{\text{II}}(\text{H}_2\text{O})(\text{trpy})]_2(\mu\text{-}[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2(\text{bpp})_2])\}^{4+}$ was disclosed to catalyze water oxidation both electrochemically and photochemically with $[\text{Ru}(\text{bpy})_3]^{3+}$ as the photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ as the electron acceptor in neutral phosphate buffer. The mechanism of water oxidation catalyzed by this unprecedented trinuclear complex was studied via density functional calculations. The calculations showed that a series of oxidation and deprotonation events take place from **A**, leading to the formation of complex **1** (formal oxidation state of $\text{Ru}^{\text{IV}}\text{Mn}^{\text{III}}\text{Ru}^{\text{III}}$), which is the starting species for the catalytic cycle. Three sequential oxidations of **1** result in the generation of the catalytically competing species **4** (formal oxidation state of $\text{Ru}^{\text{IV}}\text{Mn}^{\text{V}}\text{Ru}^{\text{IV}}$) that triggers the O-O bond formation. The direct coupling of two adjacent oxo ligands bound to Ru and Mn leads to the production of a superoxide intermediate **Int1**. This step was calculated to have a barrier of $7.2 \text{ kcal mol}^{-1}$ at the B3LYP*-D3 level. Subsequent O_2 release from **Int1** turns out to be quite facile. Other possible pathways were found to be much less favorable, including water nucleophilic attack, the coupling of an oxo and a hydroxide, and the direct coupling pathway at a lower oxidation state ($\text{Ru}^{\text{IV}}\text{Mn}^{\text{IV}}\text{Ru}^{\text{IV}}$).

Keywords: water oxidation; mechanism; density functional calculations; ruthenium; manganese; trinuclear.

1. Introduction

A promising scheme to convert solar energy into chemical energy is the water splitting driven by sunlight. Water oxidation occurs at a potential of 1.23 V vs the standard hydrogen electrode (SHE) and is both thermodynamically and kinetically very unfavorable. In photosystem II, a Mn_4Ca cluster in the oxygen evolution center (OEC) is known to catalyze the oxidation of water into molecular dioxygen.¹⁻⁵ During the past few decades, extraordinary efforts have been dedicated to the synthesis of manganese-based molecular complexes to mimic the structure and function of OEC.⁶⁻¹⁰ Other transition metals have also been used for the synthesis of water oxidation catalyst, including Ru,¹¹⁻²⁴ Ir,²⁵⁻²⁶ Fe,²⁷⁻³¹ Co,³²⁻³⁴ Ni,³⁵⁻³⁷ and Cu.³⁸⁻⁴⁰

Recently, the Llobet group disclosed the synthesis of a heterotrinnuclear Ru_2Mn complex **A** $\{[\text{Ru}^{\text{II}}(\text{trpy})]_2(\mu\text{-}[\text{Mn}^{\text{II}}(\text{bpp})_2])(\text{OAc})_2\}^{2+}$.⁴¹ This pre-catalyst undergoes water/acetate ligand exchange to form complex **A** $\{[\text{Ru}^{\text{II}}(\text{H}_2\text{O})(\text{trpy})]_2(\mu\text{-}[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2(\text{bpp})_2])\}^{4+}$ (Figure 1) that is capable of mediating water oxidation both electrochemically and photochemically.⁴¹ The photochemical reaction was performed using $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ as the sacrificial electron acceptor in neutral phosphate buffer. A turnover number of 8 was obtained in about 10 minutes. For the electrochemical reaction, the differential pulse voltammetry (DPV) study of **A** displayed a catalytic onset potential of 1.5 V.⁴¹ A related CoRu_2 complex was also reported, and the TON was estimated to be 50 using the same photochemical water oxidation condition. Since the complex water oxidation process involves the removal of four protons and four electrons, this trinuclear complex represents an elegant example that the multiple redox-active metal centers can cooperate during the four electron transfer processes. In addition, all three metals possess one or two aqua ligands. As a consequence, the high oxidation states can be accessed more easily via proton-coupled electron transfer.

To improve the efficiency of water oxidation catalysts and design new catalysts, a detailed mechanistic understanding of the reaction mechanism is of great importance. In recent years, quantum chemical calculations have been successfully applied to

elucidate the catalytic mechanism for a large number of homogeneous water oxidation catalysts.⁴² In this paper, we carried out quantum chemical calculations to delineate the mechanism of water oxidation catalyzed by this trinuclear Ru₂Mn complex. Various possible O-O bond formation pathways have been considered and compared. This study provides a particular opportunity for understanding how three transition metal centers cooperate in water oxidation.

Figure 1. Optimized structures of the trinuclear Ru^{II}₂Mn^{II} complex (**A**, sextet). Distances are given in Å. Spin densities for selected atoms are indicated in italics. Unimportant hydrogen atoms are not shown for clarity.

2. Computational details

The quantum chemical calculations were performed using the Gaussian 09 program package.⁴³ All geometries were optimized with the B3LYP-D3 functional (including Grimme's D3 dispersion)^{44,45} in combination with the SDD⁴⁶ pseudopotential for Ru and Mn as well as 6-31G (*d,p*) basis set for the C, H, O and N elements. The final and the solvation energies in water solution were obtained by performing single-point calculations on the optimized geometries using the SMD⁴⁷ continuum solvation model at the B3LYP*-D3 (with 15% Hartree-Fock exchange, including D3 dispersion and Gibbs free energy corrections from B3LYP-D3)⁴⁸ level with a larger basis set, where 6-311+G(2*df*,2*p*) were used for all atoms except for Ru and Mn (SDD). The harmonic frequencies were computed to characterize the nature of various stationary points as either minima or transition states, and also to obtain the Gibbs free energy

corrections. Singlet-point calculations were performed at the B3LYP-D3,⁴⁵ M06-D3,⁴⁹ M06L-D3,⁵⁰ TPSSH-D3,⁴⁹ TPSS0-D3(25% Hartree-Fock exchange using TPSSSTPSS and keyword IOp(3/76=0750002500)),⁵¹⁻⁵² and TPSSSTPSS-D3⁵³ levels to assess the sensitivities of redox potentials and barriers to the choice of functionals.

The pK_a values were calculated in order to determine the protonation state of all species at the working pH=7, and the experimental solvation energy of -264.0 kcal mol⁻¹ of a proton was used.⁵⁴ The Gibbs free energy correction of -6.3 kcal mol⁻¹ derived from the translational entropy of a proton in the gas phase was added.⁵⁴ The experimental solvation free energies of water (-6.3 kcal mol⁻¹)⁵⁴ and acetate (-77.0 kcal mol⁻¹)^{55,56} in aqueous solution were used. The calculated solvation free energies of water and acetate are -7.5 kcal mol⁻¹ and -69.2 kcal mol⁻¹, respectively. The experimental values for the solvation free energies of water and free anions (chloride) has also been used in our previous study on an iron-catalyzed water oxidation reaction.⁵⁷ Importantly, the use of either the experimental values or the calculated values does not alter any mechanistic conclusion. For all species except water, the concentration correction of 1.9 kcal mol⁻¹ at room temperature in water solution was added, which was derived from the change of the standard state from 1 atm (24.5 L mol⁻¹, 298.15 K) for the ideal gas to 1 M (1 mol L⁻¹) in water solution. For water, a value of 4.3 kcal mol⁻¹ was used as its standard state is 55.6 M. For the calculations of the redox potentials, the experimental absolute potential of the [Ru(bpy)₂]³⁺/[Ru(bpy)₂]²⁺ couple (1.26+4.281 V) was used as a reference,⁵⁸ which corresponds to an electron affinity of 127.8 kcal mol⁻¹. This value was used to set up the free energy diagram for the whole catalytic cycle. This kind of methodology has been documented in details in our recent review⁴² and has been successfully applied to the study of many different molecular water oxidation catalysts.^{16, 59-65}

3. Results and discussion

3.1 Redox potentials

Our investigation starts from the conversion of **A₀** (Figure **S1**) to **A** (Ru^{II}Mn^{II}) by the displacement of two acetates with four water molecules. This process was calculated to be endergonic by 3.9 kcal mol⁻¹. **A** was calculated to be a sextet, which has a high-spin Mn^{II} ($S_{\text{Mn}}=5/2$) and two low-spin Ru^{II} ($S_{\text{Ru}}=0$). This is consistent with the EPR and magnetic susceptibility results obtained for **A₀** in the acetonitrile solution, which showed a six-line signal characteristic of a high-spin Mn^{II} ion.⁴¹ The pK_as of **A** and its deprotonated form **A_{dp}** were calculated to be 5.1 and 5.6, respectively. Under the working condition of pH=7, two protons are released from the two Ru-bound water molecules in **A** to generate **A_{2dp}** (Figure **S1**). The formation of **A_{2dp}** from **A₀** is thus exergonic by 0.6 kcal mol⁻¹. In **A_{2dp}**, both Mn-bound water molecules form hydrogen bonds to the two Ru-bound hydroxides.

The one electron oxidation of **A_{2dp}** (Ru^{II}Mn^{II}) results in the generation of a septet complex **B** (Ru^I^{III}Mn^{II}Ru^{II}, Scheme **1**, Figure **S1**). The spin densities on Ru1 and Mn are 0.83 and 4.82, respectively. The antiferromagnetic coupled quintet state (5α on Mn and 1β on Ru1) is only 0.2 kcal mol⁻¹ higher in energy. During the oxidation, the electron is removed from one of the two Ru^{II} centers, rather than from the Mn^{II} center, and the oxidation potential was calculated to be 0.30 V. When the redox potential of the [Ru(bpy)₃]³⁺/[Ru(bpy)₃]²⁺ couple (1.26 V vs. SHE) was used as a reference, the formation of complex **B** is exergonic by 22.1 kcal mol⁻¹. This is followed by the one electron oxidation of the other Ru^{II} center with a potential of 0.37 V, leading to the formation of complex **C** (Ru^I^{III}Mn^{II}Ru^{II}^{III}, Figure **S1**). The high spin octet of **C** was calculated to be the most stable, and the spin densities on Ru1, Mn, and Ru2 are 0.83, 4.85 and 0.83, respectively. The sextet and quartet states are 3.7 and 0.4 kcal mol⁻¹ higher, respectively. From **C**, a proton-coupled electron transfer (PCET) oxidation takes place to generate complex **D** (Ru^I^{III}Mn^{III}Ru^{II}^{III}, Figure **S1**), associated with a potential of 0.67 V. During the oxidation, the electron is removed from the Mn^{II} center and the proton is removed from the Mn^{II}-coordinated water molecule. **D** was

calculated to be a high-spin septet, and the spin densities on Ru1, Mn, and Ru2 are 0.82, 3.90 and 0.82, respectively. The quintet and triplet states were calculated to be almost isogonic, being 0.2 kcal mol⁻¹ and 0.5 kcal mol⁻¹, respectively, higher than the septet. From these calculations, it can be seen that in this complex the oxidation of Mn^{II} is more difficult than that of Ru^{II}. The following oxidation also takes place first at the Ru^{III} center, rather than the Mn^{III} center. The oxidation of **D** to generate **1** (Ru^I^{IV}Mn^{III}Ru^{II}^{III}, Figure 2) was found to be a PCET process, with the proton released from the Ru1-bound hydroxide. The redox potential was calculated to be 0.74 V. **1** is an octet, and the spin densities on Ru1, Mn, Ru2 and O4 (Table S1) are 0.81, 3.92, 1.09 and 0.86, respectively. Consequently, a Ru^{III}-oxyl radical is produced. The sextet, quartet and doublet are 11.8, 0.4 and 0.8 kcal mol⁻¹ higher, respectively. In the sextet, an intermediate-spin Mn^{III} (2α) is presented, which makes its energy much higher than the octet state with a high-spin Mn^{III} (4α). Isomerization of **1** via proton transfer from the Mn^{III} bound water molecule to the Ru1^{III}-oxyl radical to generate **1'** (Ru^{III}Mn^{IV}Ru^{II}^{III}, Figure S3) with one Mn^{IV} center was found to be endergonic by 5.1 kcal mol⁻¹.

*Scheme 1. Conversion of **A** to **1**. Other ligands are omitted for clarity.*

Complex **1** was found to be the initial species for the whole catalytic cycle (vide infra). The one electron oxidation of **1** to form **2** (Ru^I^{IV}Mn^{III}Ru^{II}^{IV}, Figure 2) is associated with the release of two protons, one from the Ru^{II}^{III} bound hydroxide and the other from the Mn^{III} bound water molecule. The pK_as of **2**_{dpt}

$[\text{Ru1}^{\text{IV}}(\text{OH})\text{Mn}^{\text{III}}(\text{OH})_2\text{Ru2}^{\text{IV}}(\text{OH})]^{5+}$ and **2_{pt}** $[\text{Ru1}^{\text{IV}}(\text{O})\text{Mn}^{\text{IV}}(\text{OH})_2\text{Ru2}^{\text{III}}(\text{OH})]^{4+}$ (Figure S3) were calculated to be -1.7 and 6.6, respectively. The redox potential for this oxidation was calculated to be 0.98 V. **2** is a nonet, and the spin densities of Ru1, Mn, Ru2, O1 and O4 are 0.97, 3.88, 0.97, 0.97 and 0.97 (Table S1), respectively. Therefore, **2** is best described as a high-spin Mn^{III} ($S_{\text{Mn}}=2$) ferromagnetically coupled with two low-spin Ru^{III} -oxyl radicals ($S_{\text{Ru1}}=S_{\text{Ru2}}=1/2$, $S_{\text{O1}}=S_{\text{O4}}=1/2$). The septet, quintet, triplet and broken-symmetry open-shell singlet states lie at +17.7, +12.8, +6.9 and +1.2 kcal mol⁻¹ higher, respectively. Isomer **2'** (Figure S3), with a proton transfer from the Mn bound hydroxide to one of the oxyl radical in **2**, is 5.8 kcal mol⁻¹ higher than **2**.

Next, in the conversion of **2** to **3** ($\text{Ru2}^{\text{IV}}\text{Mn}^{\text{IV}}$, Figure 2), the Mn is oxidized from Mn^{III} to Mn^{IV} with a potential of 0.75 V, which is even lower than that of **1** to **2**. During the oxidation, no proton is released as the pK_a of **3_{dp}** was calculated to be 14.8. **3** is an octet, and the spin density on Mn of **3** is 2.83. The sextet, quartet and doublet, are 7.6, 12.8 and 7.1 kcal mol⁻¹ higher, respectively. Similarly, with **2**, proton transfer from Mn bound hydroxide to one of the oxygens in **3** to generate **3'** (Figure S3) is endergonic by 19.5 kcal mol⁻¹.

Then, a PCET of **3** leads to the formation of a $\text{Ru1}^{\text{IV}}\text{Mn}^{\text{V}}\text{Ru2}^{\text{IV}}$ complex **4** (Figure 2), and the redox potential for this oxidation step was calculated to be 1.54 V. Complex **4** is a septet and the spin densities on Ru1, Mn, Ru2, O1, O2 and O4 are 0.99, 1.05, 2.77, 0.69, -0.53 and 0.90, respectively. In **4**, a Mn^{IV} is antiferromagnetically coupled with an oxyl radical, which is similar to many other Mn-based water oxidation catalysts,^{62,66-72} including the oxygen evolving complex in photosystem II.⁶⁶⁻⁶⁸ The effect of spin coupling on the energy of **4** was calculated using the Noodleman approach (see supporting information for details).⁷³⁻⁷⁵ The calculated J-value is 3.1 kcal/mol, and the inclusion of the Noodleman correction decreases the energy by 1.55 kcal/mol, which is very similar to the previous study on the dinuclear Mn water oxidation catalyst.⁶⁹ In this case, a negative spin is presented in this Mn-bound oxyl radical while positive spin in the Ru-bound oxyl radicals. This kind of spin alignment would favor the following O-O bond formation by the coupling of two oxyl radicals

with opposite spin densities. The nonet (with ferromagnetic coupling between Mn^{IV} and the oxyl radical), quintet and triplet states are 13.0, 6.4 and 0.5 kcal mol⁻¹ higher, respectively.

The DPV studies of complex A in neutral phosphate buffer gave three oxidation peaks at approximately 0.60, 0.74, and 1.05 V.⁴¹ From the present calculations, these three peaks can be assigned as the oxidation of C to D (0.67 V), the oxidation of D to 1 (0.74 V), and the two electron oxidation of 1 to 3 (0.86 V), respectively. Finally, the electrocatalytic wave is observed experimentally at 1.54 V that is associated with the 3 to 4 oxidation is calculated at 1.54 V. The calculated redox potentials are in very good agreement with the experimentally reported and especially remarkable with the 3 to 4 transition responsible for water oxidation catalysis. The lower oxidation state transitions from A to B and B to C are not observed experimentally probably due to the low quality of the electrochemical response for this complex.⁴¹

It is worth mentioning here that the active species, derived from A, that are responsible for the O-O bond formation, reach formal oxidation states $\text{Ru}^{\text{IV}}\text{Mn}^{\text{V}}\text{Ru}^{\text{IV}}$. This is in good agreement with the OEC-PSII, where a formal Mn(V) is also needed in the S₄ state.⁶⁶⁻⁶⁸

Figure 2. Optimized structures of **1** (Octet), **2** (Nonet), **3** (Octet) and **4** (Septet). Distances are given in Å. Spin densities on selected atoms are indicated in red italics. Unimportant hydrogen atoms are not shown for clarity. For all structures, only the ground state is shown.

Figure 3. Energy diagram (in kcal/mol) for water oxidation. A reference potential of 1.26 V was used to set up the diagram.

3.2 O-O bond formation

O-O bond formation in water oxidation by Ru^{17-20, 76-80} and Mn^{62, 69-72, 81-86} catalysts have been widely studied by quantum chemical calculations. The two popular pathways, namely direct coupling (DC) of two adjacent oxygen units and water nucleophilic attack (WNA), were studied herein.

For the direct coupling pathway, we first considered the coupling of two adjacent oxo groups. The transition state (**TS1**) was optimized and is shown in Figure 4. **TS1** prefers to be a septet, and the two oxygen atoms that form the nascent O-O bond have opposite spins (0.60 on O1 and -0.41 on O2). This is required for an efficient O-O bond formation, and the important O1-O2 distance is 1.89 Å. **TS1** was characterized to be a true transition state with only one imaginary frequency of 136.6i cm⁻¹. The energy barrier relative to **4** was calculated to be only 0.7 kcal mol⁻¹ (Figure 3), and the total energy barrier became 7.2 kcal mol⁻¹ when the energy penalty for the formation of **4** was added. The quintet and triplet barriers were calculated to be 7.2 and 1.1 kcal mol⁻¹, respectively relative to **4**_{septet}. Downhill from **TS1**, a peroxide intermediate was expected to be formed. However, the calculations showed that an electron is transferred from the peroxide to Mn^{IV}, which leads to the formation of a superoxide bridging Mn^{III} and Ru^I^{III}. In this intermediate **Int1** (Figure 4), the O1-O2 distance is 1.32 Å, which is shorter than that of a common peroxide O-O single bond (around 1.4 Å). The spin densities are listed as following, Ru1: 0.81, Mn: 3.76, Ru2: 1.03, O1: -0.26, O2: -0.41, O4: 0.92. **Int1** lies at -13.3 kcal mol⁻¹ relative to **4**. The nonet, quintet, triplet and singlet states were calculated to be 3.4, 2.0, 0.3 and 2.8 kcal mol⁻¹ higher in energy, respectively.

Figure 4. Optimized structures of **TS1**, **Int1**, **TS1_H** and **Int1_H**. All structures are at septet state. Distances are given in Å. Spin densities on selected atoms are indicated in red italics. The imaginary frequencies of transition states are also given. Unimportant hydrogen atoms are not shown for clarity. For all structures, only the ground state is shown.

We then considered the coupling of a Ru^{II} bound oxyl radical (O4) and a Mn^{IV} bound hydroxide (**TS1_H**, Figure 4). The barrier of **TS1_H** (septet) was calculated to be +15.6 kcal mol⁻¹ higher than **TS1**, suggesting that this pathway is much less favorable. **TS1_H** was calculated to be a septet, in which the spin densities on O3 and O4 are -0.30 and 0.37, respectively. In **TS1_H**, the important O3-O4 distance is 1.87 Å. This leads to the formation of a hydroperoxide bridging Mn^{IV} and Ru^{II} (**Int1_H**, Figure 4), and this step is endergonic by 11.4 kcal mol⁻¹. Therefore, this pathway is both kinetically and thermodynamically less favorable compared with the coupling of two oxo groups.

For the alternative WNA mechanism, three scenarios were considered, namely attack on one of the two Ru^{III}-oxyl moieties (**TS1_w** and **TS1_{wH}**, Figure 5) or the Mn^{IV}-oxyl moiety (**TS1_{w'}**, Figure 5). For **TS1_w** and **TS1_{w'}**, the proton acceptors are the adjacent Mn^{IV}-oxyl and Ru^{III}-oxyl, respectively. The calculated barrier for **TS1_w** is 13.2 kcal mol⁻¹ relative to **4_{septet}** plus a separated water molecule. This is 12.5 kcal mol⁻¹ higher than that of **TS1**. At **TS1_w**, the critical O1-O_w distance is 2.00 Å. **TS1_w** prefers to be an open-shell broken-symmetry singlet, in which the two Ru moieties are

coupled with the high-spin Mn in an antiferromagnetic fashion. The triplet, quintet, and septet barriers are 5.7, 0.4, and 0.7 kcal mol⁻¹ higher, respectively. In addition, **TS1_{WH}**, with the Mn^{IV} bound hydroxide as the proton acceptor, is 6.8 kcal mol⁻¹ higher than the **TS1_w**. This suggests that the Mn^{IV}-bound oxyl group is a better proton acceptor than the Mn^{IV}-bound hydroxide. (Figure S4) Furthermore, **TS1_w'** lies at +31.3 kcal mol⁻¹ relative to **4_{septet}** plus a water molecule (Figure S4). These calculations suggest that the water nucleophilic attack pathway is not a viable option.

Figure 5. Optimized structures of **TS1_w** (Broken-symmetry Singlet), **Int1_w** (Septet), **TS1_{WH}** (Septet), **Int1_{WH}** (Septet), **TS1_w'** (Nonet) and **Int1_w'** (Septet). Distances are given in Å. Spin densities on selected atoms are indicated in red italics. The imaginary frequencies of transition state are also given. Unimportant hydrogen atoms are not shown for clarity. For all structures, only the ground state is shown.

O-O bond formation taking place at a lower oxidation state Ru1^{IV}Mn^{IV}Ru2^{IV} (**3**) has

also been taken into account. The direct coupling of a Ru^{III}-oxyl moiety and a Mn^{IV} bound hydroxide via **3-TS1** (Figure S3) has a barrier of 19.8 kcal mol⁻¹ (Figure 3) relative to **3**. The barrier is thus 12.6 kcal mol⁻¹ higher than that of **TS1** as described above. These results further confirmed that O-O bond formation takes place at the formal oxidation state of Ru1^{IV}Mn^VRu2^{IV}.

In addition to the thorough calculated energetic analysis carried out here, the generation of the intramolecular O-O bond formation is intuitively supported by the radical nature of all the neighboring M-O units at high oxidation states.

3.3 O₂ release

For the release of a triplet O₂ molecule from **Int1**, a number of pathways can be envisioned. First, the superoxide moiety dissociates from the Mn^{III} center through a transition state (**TS2** in Figure 6). We found that the first dissociation step requires that both the superoxide and the Mn^{III} center have positive spin densities. Consequently, the nonet was optimized for **TS2**, which is shown in Figure 6. The energy barrier was calculated to be 5.9 kcal mol⁻¹ relative to **Int1**, which is 1.3 kcal mol⁻¹ lower (Figure 3) than that of **TS1**. In **TS2**, the important Mn-O2 distance was calculated to be 2.50 Å, and the spin densities on Ru1, Mn, Ru2, O1 and O2 are 0.77, 3.89, 1.03, 0.54 and 0.63 respectively. **TS2** was calculated to have only one imaginary frequency of 110.3i cm⁻¹. In the resulting intermediate **Int2** (Figure 6), the Mn-O2 distance is 2.63 Å. In this step, no electron transfer occurs and the superoxide is coordinated to Ru1. **Int2** lies at +6.0 kcal mol⁻¹ relative to **Int1**. From **Int2**, partial intramolecular electron transfer from the superoxide moiety to the Ru1^{III} center leads to the formation of the **Int3** (Figure 6), which lies at -3.6 kcal mol⁻¹ relative to **Int2**. The total spin density on the dioxygen moiety increases from 1.27 in **Int2** to 1.59 in **Int3**. In addition, the O1-O2 distance decreases from 1.30 Å in **Int2** to 1.25 Å in **Int3**. The release of a dioxygen molecule from **Int3** to form **Int4** (Figure 6) is exergonic by 5.5 kcal mol⁻¹. An electronic energy scan by increasing the Ru-O distance showed a continuous increase of energy in the gas phase geometry optimization (Figure S5-1). However, transition state can be optimized in the water solution (**TS3**, Figure S5-2),

which gave a barrier of only 4.3 kcal mol⁻¹ relative to **Int2**. **Int4** prefers to be a triplet, the septet and quintet are 0.9 and 17.2 kcal mol⁻¹ higher, respectively. In **Int4**, both Mn and Ru1 were five-coordinated. Then, one electron oxidation of **Int4** results in **Int5** (Figure 6), and the electron is removed from the Ru1^{II} center with a potential of 1.09 V. In **Int5**, the spin densities on Ru1, Mn, Ru2 and O4 are 0.72, 3.89, 1.07 and 0.88, respectively. **Int5** is an octet, and the sextet, quartet and doublet state are 0.7, 6.9 and 1.0 kcal mol⁻¹ higher, respectively. Subsequently, two water molecules bind to the Ru1^{III} and Mn^{III} centers, coupling with the release of one proton to regenerate **1**, which can reentry the next catalytic cycle.

An alternative pathway is the one electron oxidation of **Int1**, leading to the formation of **Int2'** (Figure 6). The electron is removed from the superoxide moiety, and a triplet O₂ is formed in **Int2'**. The redox potential for this oxidation was calculated to be 1.37 V, which suggests the formation of **Int2'** is endergonic by 2.5 kcal mol⁻¹ from **Int1**. **Int2'** prefers to be dectet, the octet, quartet and doublet state are slightly higher in energies (lying at +0.6, +0.9 and +1.3 kcal mol⁻¹, respectively), while the sextet is 10.1 kcal mol⁻¹ higher. In **Int2'**, the spin densities on Ru1, Mn, Ru2, O1, O2 and O4 are 0.82, 3.90, 1.07, 0.80, 1.01 and 0.89, respectively. The Ru1-O1 distance is 2.13 Å. However, geometry optimization in water solution using the SMD solvation model (labeled as **Int2p'**, Figure S6) showed that the triplet O₂ dissociates from the Ru1^{III} center after the oxidation of **Int1**, and the Ru1-O1 distance increases to 3.01 Å. The release of a triplet O₂ molecule from **Int2'** also leads to **Int5**.

Figure 6. Optimized structures of **TS2** (Nonet), **Int2** (Nonet), **Int3** (Nonet), **Int4** (Triplet), **Int5** (Octet) and **Int2'** (Dectet). Distances are given in Å. Spin densities on selected atoms are indicated in red italics. Unimportant hydrogen atoms are not shown for clarity. The imaginary frequencies of transition state are also given. For all structures, only the ground state is shown.

The above discussed two pathways may compete with each other. Other possible pathways of O₂ release through water insertion into either the Ru1 center or the Mn center were found to be energetically less favorable, as discussed in the supporting information (Page S12-S14).

From Figure 3, it can be seen that the calculated total barrier at the B3LYP*-D3 level is only 7.2 kcal mol⁻¹ (from **3** to **TS1**) assuming that the electrochemical oxidation steps are not rate-limiting. The calculated value is somewhat underestimated compared with the experimental kinetic data (a TON of 12.2 in 10

minutes; Calculated from Figure 7 in Ref 41), which is about 20 kcal mol⁻¹. This may attribute to the density functional used. Singlet-point calculations at the B3LYP-D3, M06L-D3, M06-D3, TPSS0-D3 (25% HF exchange), TPSSh-D3 and TPSSTPSS-D3 levels have also been performed to evaluate how sensitive the calculated redox potentials and total barriers are regarding to the choice of the density functionals used. The calculated results are displayed in Table 1. Importantly, all functionals favor the direct coupling pathway for the O-O bond formation. The total barrier increases to 11.0 kcal mol⁻¹ when B3LYP-D3 was used, and further to 15.4 kcal mol⁻¹ when M06-D3 was used. The calculated onset potentials at the B3LYP*-D3, M06L-D3 and TPSSh-D3 level are 1.54 V, 1.44 V and 1.51 V, respectively, which are consistent with the experiment results (1.50 V).⁴¹ However, the B3LYP-D3, M06-D3 and TPSS0-D3 functionals gave slightly higher values. It seems that density functionals with more HF exchange give slight higher values of redox potentials than those with less HF exchange, as found in our previous study on mononuclear iron water oxidation catalyst.⁵⁷ It is also plausible that the oxidation of **3** to **4** is the rate-limiting step in the photochemical oxidation since the formation of **4** is endergonic by 6.5 kcal/mol. This large endergonicity results in a much slower electronchemical oxidation than the normal exergonic electronchemical oxidation. A stronger oxidant than [Ru(bpy)₃]³⁺ should favor this step, and lower the total barrier. Indeed, the electrochemical oxidation has a onset potential of 1.50 V,⁴¹ which is higher than the potential of [Ru(bpy)₃]³⁺/[Ru(bpy)₃]²⁺ (1.26 V).

Table1. Comparson of the redox potentials and barriers with different functionals.

	Redox Potential(V)			Total Barrier(kcal mol ⁻¹)		
	2/1	3/2	4/3	DC _{OO} ^a	DC _{OOH} ^b	WNA
B3LYP*-D3	0.98	0.75	1.54	7.2	22.8	20.2
B3LYP-D3	1.13	0.97	1.70	11.0	27.0	25.2
M06L-D3	0.82	0.32	1.44	6.1	17.9	22.7
M06-D3	0.99	1.29	1.83	15.4	32.4	32.1
TPSS0-D3 ^c	1.23	1.14	1.83	13.9	32.5	35.0
TPSSh-D3	1.02	0.59	1.51	6.2	23.1	20.6
TPSSTPSS-D3	0.89	0.21	1.21	0.7	17.3	14.3

^a direct oxo-oxo coupling mechanism.

^b direct oxo-hydroxide coupling mechanism.

^c with 25% HF exchange.

Here we used the reorganization energy of 17.2 kcal/mol and second-order rate constant of $4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the self-exchange electron transfer between $[\text{Ru}(\text{bpy})_3]^{3+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ as a reference,⁸⁷ the barrier ($\Delta G^\ddagger$) for the oxidation of **3** by $[\text{Ru}(\text{bpy})_3]^{3+}$ was calculated to be 12.7 kcal/mol using the Marcus theory⁸⁸ by assuming the same reorganization energy for these two different electrochemical reactions.

$$\Delta G^\ddagger = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \quad (1)$$

where λ is the reorganization energy and ΔG^0 is the driving force.

The apparent barrier under the experimental condition ($5 \times 10^{-4} \text{ M}$ for the concentration of $[\text{Ru}(\text{bpy})_3]^{3+}$)⁴¹ can be estimated to be 17.2 kcal/mol when the concentration correction was taken into account. This value can be considered to be in reasonably good agreement with the experimental barrier of about 20 kcal/mol.⁴¹ The oxidation of **3** by $[\text{Ru}(\text{bpy})_3]^{3+}$ may have larger reorganization energy than the self-exchange reaction between $[\text{Ru}(\text{bpy})_3]^{3+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$. If a reorganization energy of 23.06 kcal/mol (1 eV) was used, the apparent barrier increases slightly to 18.5 kcal/mol. It should be pointed out that more accurate estimation of the rate for this electrochemical rate for this step requires advanced calculations of reorganization energies (reactant, product, and solvent), driving force, the electronic coupling, and the proton transfer interface properties,⁸⁹⁻⁹¹ which is beyond the scope of the present study.

4. Conclusion

In the present work, we have studied the water oxidation mechanism catalyzed by the heterotrinuclear complex $\text{Ru}_2\text{Mn}-(\text{H}_2\text{O})_4$ (**A**) using density functional calculations. The whole catalytic cycle (Scheme 2) including relevant redox intermediates and redox potentials was calculated.

Scheme 2. Suggested catalytic cycle for water oxidation by the heterotrinnuclear Ru₂Mn complex on the basis of calculations.

Water oxidation commences from the formal oxidation state Ru^I^{IV}Mn^{III}Ru^{II}^{III} (**1**). A Ru^{III}-oxyl complex **1** was generated from **A** through a number of deprotonation and oxidation events. From **1**, one electron oxidation of Ru^{II} leads to **2** with a formal oxidation state of Ru^I^{IV}Mn^{III}Ru^{II}^{IV}, and this process is coupled with the release of two protons. Then, one electron oxidation of the Mn^{III} center in **2** results in **3** (Ru^I^{IV}Mn^{IV}Ru^{II}^{IV}). Next, a PCET oxidation of **3** generates **4** (Ru^I^{IV}Mn^{IV}Ru^{II}^{IV}) with a potential of 1.54 V. Complex **4** is capable of triggering O-O bond formation through the direct coupling of a Ru-oxo and a Mn-oxo. The direct coupling of two oxo units leads to the superoxide intermediate **Int1**, with a total barrier of 7.2 kcal mol⁻¹ at the B3LYP*-D3 level when assuming the electrochemical oxidation of **3** is ultrafast. Other O-O bond formation mechanisms, including the WNA mechanism, the direct coupling of an oxo and a hydroxide, and the direct coupling at a lower oxidation state were calculated to be much less favorable.

The O₂ release may take place directly from **Int1** or after a one electron oxidation of

Int1. For the former pathway, the superoxide first dissociates from the Mn center in **Int1** via **TS2**, which generates a Ru1-bound superoxide intermediate **Int2**. The intramolecular electron transfer from the superoxide to Ru1 leads to the formation of **Int3**, which has a triplet O₂ bound to the Ru1 center. Subsequently, O₂ is released, followed by another one electron oxidation to form **Int5**. Finally, two water molecules bind to Ru1 and Mn, concomitant with a proton release to regenerate **1**. The one electron oxidation of **Int1** results in the direct dissociation of the dioxygen moiety from the Mn center and the formation of a triplet O₂ bound to the Ru1 center (**Int2'**). **Int2'** can be converted into **Int5** after the release of O₂. These two pathways about O₂ evolution may compete with each other as they were both found to be quite facile. Other possible pathways of O₂ release via water insertion are energetically less favorable.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21503083 and 21873031) and the Fundamental Research Funds for the Central Universities (2017KFKJXX014). AL thanks support from MINECO, FEDER and AGAUR (CTQ2016-80058-R and 2017-SGR-1631).

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Graphical abstract for

Quantum Chemical Study of the Mechanism of Water Oxidation Catalyzed by a Heterotrinnuclear Ru_2Mn Complex

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