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Iron-Catalyzed Water Oxidation: O–O Bond Formation via Intramolecular Oxo–Oxo Interaction

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Dedicated to the 100th anniversary of the Department of Chemistry at Nankai University

Abstract: Herein, we report the importance of structure regulation on the O-O bond formation process in binuclear iron catalysts. Three complexes, $[Fe_2(\mu-O)(OH_2)_2(TPA)_2]^{4+}$ (1), $[Fe_2(\mu-O)(OH_2)_2(6-HPA)]^{4+}$ (2) and $[Fe_2(\mu-O)(OH_2)_2 (BPMAN)J^{4+}$ (3), have been designed as electrocatalysts for water oxidation in 0.1 M NaHCO₃ solution (pH 8.4). We found that 1 and 2 are molecular catalysts and that O-O bond formation proceeds via oxo-oxo coupling rather than by the water nucleophilic attack (WNA) pathway. In contrast, complex 3 displays negligible catalytic activity. DFT calculations suggested that the anti to syn isomerization of the two highvalent Fe=O moieties in these catalysts takes place via the axial rotation of one Fe=O unit around the Fe-O-Fe center. This is followed by the O–O bond formation via an oxo–oxo coupling pathway at the Fe^{IV}Fe^{IV} state or via oxo-oxyl coupling pathway at the Fe^{IV}Fe^V state. Importantly, the rigid BPMAN ligand in complex 3 limits the anti to syn isomerization and axial rotation of the Fe=O moiety, which accounts for the negligible catalytic activity.

Introduction

Water oxidation $(2H_2O \rightarrow O_2 + 4H^+ + 4e^-)$ is an essential step in both natural and artificial photosynthesis, because it is the ideal electron/proton source for chemical fuels production.^[1] To date, numerous transition-metal complexes (such as Ru,^[2] Ir,^[3] Mn,^[4] Co,^[5] Fe,^[6] Ni^[7] and Cu^[8]) have been used as molecular water oxidation catalysts (WOCs) to lower the kinetics barriers of this reaction. These previous studies have partially revealed the catalytic mechanism of water oxidation. For example, two types of O–O bond formation mechanism, water nucleophilic attack (WNA) and interaction of two M-O units (I2M), are proposed for guiding the catalyst design.^[1f] However, water oxidation is still the bottleneck for artificial photosynthesis because of the

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 the author(s) of this article can be found under: https://doi.org/10.1002/anie.202100060. inherent difficulty of water oxidation catalysis, lack of enough understanding of multielectron/multiproton transfer ($4e^{-/}$ $4H^+$ for water oxidation) and O–O bond formation. To develop earth-abundant catalysts with performance as well as or better than precious materials is one of the challenges for water oxidation catalysis. Precise understanding of catalytic mechanisms and identification of structures and oxidation states of transient species during catalytic turnover are crucial for rational catalyst design.

Iron is considered as the most attractive candidate for water oxidation due to its cheapness, abundance and biocompatibility. Collins and co-workers firstly reported a monoiron complex (Fe-TAML) for catalytic water oxidation at pH 0.7 with Ce^{IV}(CAN) as sacrificial oxidants.^[6a] Fillol and Costas described a family of neutral tetradentate ligands based iron complexes as WOCs in which the $Fe^{V}(O)(OH)$ was proposed as the key intermediate for O-O bond formation via water nucleophilic type mechanism.^[6b] Meyer and Dhar also demonstrated that high valent intermediate of Fe^V=O can promote the O-O bond formation by WNA pathway with unsatisfying efficiency.^[6c,d] Recently, Lloret-Fillol and Costas found that highly active Fe^V=O can cause the collapse of itself skeleton via hydrogen atom transfer and pointed out the possible stability problems of mononuclear Fe-based catalyst.^[9] To further tune the O–O bond formation step, di- or polynuclear iron-based WOCs also appeared on the research.^[10] Najafpour and co-workers first found that dinuclear $[Fe_2(\mu\text{-}O)(OH_2)_2(TPA)_2]^{4+}$ was six times faster than mononuclear [Fe(TPA) (OTf or Cl)₂] with Ce^{IV} as oxidant.^[10a] However, Sakai and his co-workers reported an analogous possessing TPA ligands could be dissociated into more active single Fe-site catalyst when lowering the pH.^[10b] Interestingly, Que and his-co-workers reported a (µ-oxo)diiron(IV) complex supported by a pentadentate ligand could activate H₂O via proton-coupled electron transfer (PCET) to generate the hydroxyl radical. Unfortunately, the generated hydroxyl radical was consumed by the solvent, acetonitrile, and no O₂ or H₂O₂ was detected.^[11] Recently, Masaoka developed a highly efficient pentanuclear iron catalyst with TOF of 1900 s^{-1} , in which the charge is effectively distributed on multi-irons to improve the catalytic performance and O-O bond formation was proposed via the coupling of two terminal oxo groups.^[10e, 12] The stability of these Fe-based molecular catalysts is also a challenge because the foamed high valent Fe=O could abstract the hydrogen atom from the ligand.^[13] Above all, the study of iron catalyzed water oxidation has significant advance and the catalytic activity is strongly dependent on the ligand architecture and iron nuclearity. The further studies on key intermediates and O-

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(a)

O bond formation mechanism are helpful to regulate its catalytic activity and design new catalysts.

According to the principle of microreversibility, wellstudied O-O bond cleavage in oxygen activation via diiron complexes can give us more inspiration to explore the detail of O-O bond formation in water oxidation. Soluble methane monooxygenase (sMMO) which includes diiron active site can efficiently activate oxygen and subsequently form active intermediate.^[14] Now, groups of Que and Kodera have extensively studied O-O bond cleavage by designing the sMMO models.^[15] Que and co-workers have reported that intermediate of (µ-oxo)(µ-hydroperoxo)diiron(III,III) can turn into (µ-oxo)(hydroxo)(oxo)diiron(IV,IV) through cleavage of peroxide bond, and the latter can undergo proton transfer to yield [O=Fe^{IV}-O-Fe^{IV}=O] intermediate in the presence of base (Scheme 1 a).^[15d,h] The high-valent diiron intermediate $[O=Fe^{IV}-O-Fe^{IV}=O]$ has also been described by Kodera and co-workers through reacting corresponding diiron(III) complex with H₂O₂ and Et₃N, and it was in thermal equilibrium with its $(\mu$ -oxo) $(\mu$ -1,2-peroxo)diiron(III) isomer (Scheme 1b).^[15f,16] Interestingly, O-O bond is formed in this thermal equilibrium via Fe^{IV}=O rather than Fe^V=O which is extensively proposed in mononuclear iron modulated water oxidation catalysis. So, this encourages us to explore whether the reverse O-O bond formation can be achieved through the coupling of two Fe^{IV}=O moieties. Structureactivity relationship can usually provide pivotal and solid mechanism information, which can be used to study O-O bond formation. As designed in Scheme 1c, while two terminal Fe^{IV}=O moieties initially locate at anti position in

[O=Fe^{IV}-O-Fe^{IV}=O] intermediate, they could get close to each other by rotating axially around the Fe-O-Fe and further couple in a relatively flexible structure. When the molecular structure becomes rigid, the rotation of Fe^{IV}=O will be limited, making them difficult to couple face-to-face, and the catalyst would have lower activity. To verify this proposal, we employed $[Fe_2(\mu-O)(OH_2)_2(TPA)_2]^{4+}$ (1), $[Fe_2(\mu-O)(OH_2)_2(6-$ HPA)]⁴⁺ (2) and $[Fe_2(\mu-O)(OH_2)_2(BPMAN)]^{4+}$ (3) as electrocatalysts to catalyze water oxidation in an alkaline condition. Complexes 1 and 2 exhibit higher activity among the three complexes in NaHCO₃ solution (pH 8.4), while complex 3 is inactive under the form of Fe^{IV}Fe^{IV} species. As designed, rigid BPMAN architecture in 3 limits the axial rotation of $Fe^{IV}=O$ and further prevents the coupling of two Fe^{IV}=O. Combined with experimental results and DFT calculations, O-O bond formation via face-to-face coupling between two Fe^{IV}=O was confirmed and thus provides a direction for the design of molecular catalysts and the regulation of catalytic efficiency.

Results and Discussion

Solid-state structures and catalytic species for three diiron complexes. The synthetic details are listed in SI. The crystal structures of three diiron(III) complexes designed by subtle modification of ligand are shown in Figure 1.^[17] Similar to the literature,^[10a, 16] the two Fe atoms are separated by 3.567 Å and 3.601 Å, with an Fe-O-Fe angle of 169.7° and 179.0°, of complex 1 and complex 2, respectively. Complex 3 with inflexible BPMAN ligand shows shorter Fe1...Fe2 distance (3.201 Å) which is closer to the Fe…Fe distance (3.221(6) Å)of [Fe2(BPMAN)(µ-OH)-(µ-O2CPhCy)](OTf)2,^[18] and an angle with bridge O1 (XFe1-O1-Fe2) at 129.0°. The two

(b)

(d)

Complexes

Fe1 --- Fe2 (Å)

∠Fe1-O1-Fe2 (°)

∠02-Fe1Fe2-O3 (°)

crystal data, involving the distance between two iron atoms (Fe1...Fe2),

the angle \measuredangle Fe1-O1-Fe2 and the dihedral angle formed by four atoms



Scheme 1. Transformation of µ-oxo-µ-peroxodiiron(III) to µ-oxodioxodiiron(IV) in O₂ activation by Que (a) and Kodera (b); The proposed alternative O-O bond formation in this work (c).

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with Fe1-Fe2 as the axis ($\angle O2$ -Fe1Fe2-O3).

3.56

169.

116.5

179.0

173.0

3

3.201

129.0

166.1

 H_2O molecules in the structure of 1–3 all bind in an *anti* fashion with respect to the diiron vector. In particular, the difference in ligand flexibility and coordination geometry among 1–3 provides a research platform for understanding the relationship between structure and catalytic activity and exploring the details of mechanism.

$$H_2O-Fe^{III}-O-Fe^{III}-OH_2 \xrightarrow{K_1} H_2O-Fe^{III}-O-Fe^{III}-OH + H^+$$
 (1)
 $H_2O-Fe^{III}-O-Fe^{III}-OH \xrightarrow{K_2} HO-Fe^{III}-O-Fe^{III}-OH + H^+$ (2)

We firstly determined the pK_a values of the aqua ligand of **1–3** [Eq. (1)–(2)] by potentiometric titration. The pK_{a1} values are 4.41, 4.93 and 4.96 for $\mathbf{1}_{\rm H_2O/H_2O},\,\mathbf{2}_{\rm H_2O/H_2O}$ and $\mathbf{3}_{\rm H_2O/H_2O},$ respectively. The pK_{a2} values are 5.22, 5.81 and 6.10 for $\mathbf{1}_{\rm H_2O/HO}, \mathbf{2}_{\rm H_2O/HO}$ and $\mathbf{3}_{\rm H_2O/HO},$ respectively (Figures S4–S6 and Table S2). It can be found that as the rigidity of the ligand increases, the acidity of the aqua ligand gradually decreases. To a certain extent, this indicates that the chemical reactivity of the aqua ligand is sensitive to the regulation of the ligand. According to the pK_{a2} values, the HO-Fe^{III}-O-Fe^{III}-OH species is the dominant existence at pH>8 buffer solution (Figures S4-S6). In terms of acetate,^[19] phosphate^[20] and sulphate^[10b,20] could play as bridge ligand to inhibit the catalytic efficiency by occupying the coordination sites of water molecules, diiron(III) complexes in 0.1 M NaHCO₃ (pH 8.4) solution was applied for electrocatalytic water oxidation investigation.[21]

Electrochemical behavior and oxygen evolution of diiron complexes 1–3. Figure 2 shows the CVs of 0.5 mM complex 1– 3 in 0.1 M NaHCO₃ (pH 8.4) using BDD electrode. For complex 1, on the cathodic direction, an irreversible cathodic process at $E_{\rm pc} = -0.23$ V vs. NHE was observed in the CV, and an irreversible anodic process at $E_{\rm pa} = 0.40$ V vs. NHE was observed in the reverse scan (Figure S8, with peak–peak splitting $\Delta E_{\rm p} = 630$ mV). When the CV was measured at



Figure 2. CVs recorded in 0.1 M NaHCO₃ (pH 8.4) solution using a BDD electrode without (black line) and with 0.5 mM **1** ((a) red line), 0.5 mM **2** ((b) blue line), and 0.5 mM **3** ((c) green line); the scan rate was 100 mVs⁻¹.

different scan rates, the peak currents varied linearly with the square root of the scan rate (Figure S9a), which indicates a diffusion-controlled process. This is assigned as the oneelectron reduction of Fe₂(III,III) to Fe₂(III,II). After two irreversible oxidative processes, the CV of 0.5 mM complex 1 exhibited a significant catalytic activity, during the scanning at 100 mV s^{-1} from 0.24 to 2.0 V vs. NHE (Figure 2a, Figure S10). CVs were further recorded at different scan rates and the resulting normalized catalytic currents increased with decreasing scan rate (Figure S9b), consistent with a water oxidation catalysis process. The onset potential for water oxidation appears at 1.57 V vs. NHE with an overpotential of \approx 830 mV followed by two oxidative waves. When complex 2 was used as WOC under the same condition, only one irreversible catalytic process was observed at 1.76 V vs. NHE (Figure 2b, Figures S11 and S12b) and the catalytic current is lower than 1. Complex 3 displays two oxidative waves at 1.36 and 1.64 V vs. NHE (Figure 2c, Figure S13), but normalized catalytic currents of 3 nearly keep constant at different scan rates (Figure S14), indicating that complex 3 cannot catalyze water oxidation. Additionally, simple Fe³⁺ ion catalyzed water oxidation was excluded by control experiments. 1.0 mM of $Fe(NO_3)_3$, $Fe(ClO_4)_3$ and $FeCl_3$ were examined under identical conditions, respectively (Figure S15). All \mbox{Fe}^{3+} ions showed no activity towards water oxidation indicating that the observed catalytic activity is not caused by free Fe³⁺ ions or formed iron oxides which may possibly exist during catalysis.

The oxygen evolution was further confirmed by controlled-potential electrolysis (CPE) (Figure 3a) using a 2 cm^2 BDD disk working electrode. For CPE at 1.57 V vs. NHE, complex 1 exhibits the highest catalytic current density of 0.7 mA cm^{-2} , followed by complex 2 with 0.3 mA cm^{-2} and complex 3 shows negligible $30 \,\mu\text{A}\,\text{cm}^{-2}$ equivalent to blank current. The dissolved oxygen was also measured by a calibrated Ocean Optics FOXY probe during CPE (Figure 3b). The concentration of O₂ dissolved in the solution phase increased from 54 µM to 301 µM for 1, from 54 µM to 180 µM for 2 and negligible for 3. For both 1 and 2, the Faraday efficiency for the O_2 evolution is above 90% in initial 5 minutes (Table S1). The oxygen evolution rate for 1 is about 2 times faster than 2, and 3 is inactive toward catalytic water oxidation, indicating that the catalytic activity is strongly dependent on the choice of ligand and the regulation of the ligand framework can achieve tuning its catalytic performance.

The stability of **1** and **2** during the electrocatalytic process was further examined by electrode analysis after long time bulk electrolysis (Figure S16). The morphology of electrode did not change before and after electrolysis in scanning electron microscopy (SEM) images (Figure S17), which indicated that there was no Fe_xO_y formation during the electrocatalytic process. Moreover, X-ray photoelectron spectroscopy (XPS, Figure S18) analysis indicated that no Fe species such as Fe_xO_y were deposited on the electrode surface, and rinse tests also showed that there was no active species attached to the electrode surface (Figure S19). CV and UV-vis absorption of the solution after electrolysis was consistent with the fresh solution (Figures S20–S22), indicat-

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Figure 3. a) Controlled-potential electrolysis with blank solution (black line) and 0.5 mM 1 (red line), 0.5 mM 2 (blue line), and 0.5 mM 3 (green line) with BDD disk working electrode (2 cm^2) in 0.1 M NaHCO₃ (pH 8.4) solution at 1.57 V vs. NHE. b) The O₂ evolution during the CPE with blank solution (black line), 0.5 mM 1 (red line), 0.5 mM 2 (blue line), and 0.5 mM 3 (green line) was measured with a fluorescence probe.

ing the species in solution was robust toward the bulk electrocatalysis, and this was further confirmed by the constant CV shape in multiple CVs scan (Figure S23). All experimental results indicate that both complexes **1** and **2** are the stable molecular electrocatalyst for water oxidation under the conditions in this work rather than nanoparticles, despite the difficulty of definitively excluding a colloid material.

Water oxidation kinetics and mechanistic analysis. According to the above discussion, **1** and **2** are able to act as homogeneous catalysts to electrocatalyze water oxidation, while **3** is catalytic silence, although all these three compounds, **1–3**, could generate corresponding high-valent Fe^{IV}Fe^{IV} intermediates via two-electron oxidation (Figures S24–S26). The currents of both the diffusion-controlled waves and catalytic waves for water oxidation by **1** and **2** are linearly dependent on the concentration of the catalysts, [Cat.], (Figures S27, S28). This suggests that the irreversible processes at -0.23 V (in **1**) and -0.26 V (in **2**) vs. NHE for the Fe₂^{III,III/III,II} couple should obey the Randles-Svecik equation in Equation (3) (Figures S8, S9a, S12a and S29) and the

 $i_{\rm d} = 0.496 n_{\rm d} FA[{\rm Cat.}] \sqrt{n_{\rm d} \alpha F v D_{\rm cat}/RT}$

tion (4),^[22]

current of the catalytic wave could be expressed by Equa-

$$\dot{u}_{\text{cat}} = n_{\text{cat}} FA[\text{Cat.}] \sqrt{k_{\text{obs}} D_{\text{cat}}}$$
(4)

where F is the Faraday constant, A is the electrode surface area, i_{d} is the peak current of the diffusion-controlled wave, i_{cat} is the peak current of the catalytic wave, [Cat.] is the bulk concentration of the diiron catalyst, D_{cat} is the diffusion coefficient of the catalyst, $n_d = 1$ is the number of electrons transferred in this diffusion-controlled process, $\alpha = 0.5$ is the transfer coefficient of the catalyst and $n_{cat} = 4$ is the electrochemical stoichiometry for water oxidation. In order to eliminate background interference, the catalytic current is corrected by subtracting the background current (Figure S30) at the same potential, marked as $i_{\text{cat'}}$. According to the plot of $i_{\text{cat'}}/i_{\text{d}}$ versus $1/\sqrt{v}$ (Figure S31), the observed rate constant for water oxidation catalysis at 1.89 V vs. NHE, k_{obs} , was determined as 0.55 s^{-1} for **1** and 0.04 s^{-1} for **2**. This apparent catalytic efficiency (k_{obs}) is consistent with the oxygen evolution rate observed in the bulk electrolysis experiment in which 1 is much faster than 2, and 3 is almost catalytic silence. The catalytic performance of **1** and **2** is comparable with mostly reported Fe-based WOCs (Table S3). The kinetics of water oxidation are also investigated in D₂O and the resulted kinetic isotope effect (KIE = $k_{cat,H_2O}/k_{cat,D_2O}$) of catalysts 1 and 2 are 1.23 and 1.12, respectively (Figures S32, S33). The observed KIE is in contrast to the single-site $Ru^{V=}$ O cases^[2n,23] in which the remarkable KIE is attributed to atom-proton transfer (APT) with O-O bond formation. Both the KIE and the catalytic behavior differences among 1-3 indicate that WNA pathway of O-O bond formation via single site $Fe^{IV} = O$ or $Fe^{V} = O$ can be excluded. More crucially, more details on the O-O bond formation could be obtained by understanding the special case 3. Complex 3 has similar electrochemistry oxidation behavior in E-pH diagram as catalyst **1** (Figures S24, S26), indicating that $O=Fe^{IV}-O-Fe^{IV}=$ O species with rigid BPMAN ligand is inactive for O-O bond formation, because two terminal Fe^{IV}=O moieties of O=Fe^{IV}-O-Fe^{IV}=O initially locate at *anti* position. While the Fe^{IV}=O moieties with flexible ligand could rotate axially around the Fe–O–Fe. This results in the direct coupling of two Fe^{IV}=O to form O-O bond and further exhibit the ability of water oxidation. This process is a reverse process of oxygen activation reported by both Que^[15h] and Kodera.^[15f] In O₂ activation, Kodera suggested that a syn-dioxo form of catalyst 2 was transformed into anti-dioxo form through a t-oxo-di(µoxo)diiron(IV) transition state.^[15f,j]

The DFT calculations^[24] were performed to further explain the different catalytic activity of **2** and **3**. For these dinuclear iron complexes with a bridging oxo ligand, the more stable antiferromagnetically coupled state^[25] was considered and presented. The protonation state of the diferric complex **2** at the working pH 8.4 was first identified. The pK_{a1} and pK_{a2} of **2** with two water molecules coordinated were calculated to be 4.9 and 6.8, respectively. These two values are in excellent agreement with our experimental data (4.93 and 5.81). This suggested that the most stable form of **2** has two hydroxide ligands in *anti* position (labeled as **2^{III,III}**), with a total charge

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of +2. The electronic structure of $2^{\text{III,III}}$ can be described as a featuring a broken-symmetry open-shell singlet with the two high spin ferric ions (S = 5/2) interacting in an antiferromagnetic fashion. The spin densities on the two iron ions are 4.09 and -4.09, respectively.

The oxidation of $2^{III,III}$ was calculated to a proton-coupled electron transfer process, with a potential of 1.20 V vs. NHE, leading to the formation of a doublet complex $2^{III,IV}$ (pK_a of 6.2 for its protonated form). With a reference potential of 1.57 V vs. NHE (experimental potential for CPE), this step was calculated to be exergonic by 8.5 kcal mol⁻¹ (Figure 4). The electronic structure of $2^{III,IV}$ can be interpreted as a high



Figure 4. Gibbs energy diagram (in kcalmol⁻¹) at the B3LYP*-D3 level for water oxidation catalyzed by **2**.

spin Fe^{III} ion (S = 5/2) antiferromagnetically coupled to the high spin Fe^{IV} ion (S = 2). Further PCET oxidation of $2^{III,IV}$ (potential of 1.32 V vs. NHE) affords an open-shell singlet complex $2^{IV,IV}$, which has two antiferromagnetically coupled Fe^{IV} ions (S=2 for each iron). The Mulliken atomic spin densities on the two iron ions become 3.13 and -3.13, respectively, while they are 0.43 and -0.43 on the two terminal oxygen atoms, respectively. In 2^{IV,IV}, the two oxo groups are in anti position, and an anti to syn isomerization has to take place via the axial rotation of one of the two Fe^{IV} = O moieties. The transition state for this process has been optimized and labeled as 2-TS1 (Figure 5), which has a barrier of 19.2 kcal mol⁻¹ relative to $2^{IV,IV}$, and this isomeric formation of **2-Int1** is endergonic by 3.3 kcalmol^{-1} . In **2-TS1**, both O1 and O2 become the bridging ligands, which results in the formation of a hexa-coordinated Fe1 and a hepta-coordinated Fe2. From 2-Int1, O-O bond formation proceeds via the coupling of the two antiferromagnetically coupled oxo/oxyl groups (2-TS2, Figure 5), similarly to the pentanuclear iron catalyst,^[12] and the heterotrinuclear MnRu₂ catalyst.^[26] The barrier for 2-TS2 was calculated to be 11.0 kcal mol⁻¹ relative to 2-Int1. 2-TS2 was characterized to have an imaginary frequency of 471.3i cm⁻¹, which corresponds to the O–O bond formation. In 2-TS2, the nascent O-O distance is 1.91 Å, and the atomic spin densities on O1 and O3 are 0.48 and -0.51, respectively. The generation of the diferric peroxide intermediate **2-Int2** is exergonic by 9.9 kcalmol⁻¹ from **2-Int1**.



Figure 5. Structures of key transition states for O–O bond formation starting from $2^{V,V}$ and $2^{V,V}$. Distances are given in Angstrom, while spin densities on key atoms are indicated in red italics.

O-O bond formation at a higher oxidation state has also been considered. Further one-electron oxidation of $2^{IV,IV}$ to produce $2^{IV,V}$ (total charge of + 3) is associated with a potential of 1.68 V vs. NHE. With an applied potential of 1.57 V vs. NHE, this process is endergonic by 2.5 kcal mol⁻¹. The anti to syn isomerization of $2^{IV,V}$ now becomes more favorable, the structure of the corresponding transition state 2-TS1' is displayed in Figure 5. The barrier for 2-TS1' was calculated to be only 10.2 kcal mol⁻¹ relative to $2^{IV,V}$. A plausible reason is that the charge repulsion between the two metal centers (IV, V vs. IV, IV) becomes larger, which makes the dissociation of the bridging O1 from Fe2 easier. This is evidenced by the significantly longer Fe2-O1 and Fe2-O2 distances in 2-TS1' (2.28 Å and 2.61 Å) compared with those in 2-TS1 (2.20 Å and 2.08 Å). In addition, this isomerization to form **2-Int1'** becomes exergonic by $2.1 \text{ kcal mol}^{-1}$. Similarly, the following O-O bond formation by the coupling of the two antiferromagnetically coupled oxo/oxyl groups via 2-TS2' has a very facile barrier of 9.3 kcal mol^{-1} relative to 2-Int1'. This leads to the production of a diferric superoxide intermediate 2-Int2', which can also be generated by the one-electron oxidation of 2-Int2 (potential of 0.59 V vs. NHE). The alternative water nucleophilic attack on 2-Int1' (2-TS3' in Figure S34 in SI) has also been considered. However, its barrier was found to be 23.4 kcalmol⁻¹ relative to 2-Int1' plus a water molecule, and the total barrier becomes 23.8 kcal mol^{-1} when the energy cost for the formation of **2-Int1'** is added. This is much higher than that via the oxo-oxo coupling. From 2-Int2', the coordination of a water molecule to Fe1 to form **2-Int3** is endergonic by 7.4 kcal mol^{-1} . In the subsequent step, a PCET oxidation takes place to afford 2-Int4, with a potential of 0.08 V vs. NHE. Finally, the coordination of

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a second water molecule and the release of O_2 and a proton regenerate $2^{III,III}$ for the next water oxidation cycle.

From Figure 4, it can be seen that the O–O bond formation prefers to take place in the oxidation state of $Fe_2^{IV,V}$ under the experimental condition. The *anti* to *syn* isomerization turns out to be the rate-limiting step, with a total barrier of 12.7 kcalmol⁻¹, which is lower than that in the oxidation state of $Fe_2^{IV,IV}$ (19.2 kcalmol⁻¹). For complex 3, the calculations showed that the two PCET oxidations to form $3^{IV,IV}$ are facile under the experimental condition. However, the *anti* to *syn* isomerization has a very high barrier of 32.5 kcalmol⁻¹ (Figure S35 in SI), due to the usage of a too rigid BPMAN ligand. The one-electron oxidation of $3^{IV,IV}$ also has a very high potential of 1.92 V vs. NHE.

Based on the experimental results and DFT calculations discussed above, we can propose the following water oxidation mechanism by diiron(III) complexes (Figure 6). The



Figure 6. Proposed mechanism of complexes 1 and 2 catalyzed water oxidation in 0.1 M NaHCO₃ (pH 8.4).

initial diiron(III) species, HO–Fe^{III}–O–Fe^{III}–OH, was oxidized to O=Fe^{IV}–O–Fe^{IV}=O by losing two electrons and two protons. The formed O=Fe^{IV}–O–Fe^{IV}=O can trigger the O–O bond formation via intramolecular oxo/oxo coupling, or it can be further oxidized to a higher valent intermediate O=Fe^{IV}– O–Fe^V=O, and then form an O–O bond via intramolecular oxo/oxyl coupling. What needs to be pointed out here is that the O–O bond formation requires the *anti-* to *syn-* configuration conversion between two Fe=O moieties. This is consistent with the results observed through the regulation of the ligand skeleton among **1**, **2** and **3**. After the O–O bond formation, the obtained Fe₂O₂ intermediate could be further oxidized to release the O₂ to close the catalytic cycle under the catalytic conditions.

Conclusion

Inspired by the O–O bond breaking in soluble methane monooxygenase (sMMO) and its diiron models, we have investigated the possibility of diiron catalyzed O–O bond formation. Three diiron(III) complexes were intentionally elected as water oxidation catalysts, in which $[Fe_2(\mu-O)-(OH_2)_2(TPA)_2]^{4+}$ (1) and $[Fe_2(\mu-O)(OH_2)_2(6-HPA)]^{4+}$ (2) are active for catalyzing water oxidation. The suggested mechanism is displayed in Figure 6. O–O bond formation was achieved via intramolecular oxo/oxo or oxo/oxyl coupling and thus it required the spatial position match of the two Fe=O. This feature provides a possibility to regulate the catalytic reactivity. The experimental results show that the tuning of the strength of ligand rigidity can effectively regulate the energy barrier of the O–O bond formation, for example, $[Fe_2(\mu-O)(OH_2)_2(BPMAN)]^{4+}$ (3) with rigid ligand has almost no catalytic activity. This work clarifies the bimetallic cooperative effect on the O–O bond formation and provide the inspiration for molecular design and catalytic regulation on iron catalyzed water oxidation. Further experiments are focused on developing new catalysts based on the mechanistic insight disclosed in this work, particular to reduce the overpotential and enhance the catalytic activity.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: artificial photosynthesis \cdot iron catalysts \cdot O-O bond formation \cdot water oxidation

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Water Oxidation

H.-T. Zhang, X.-J. Su, F. Xie, R.-Z. Liao,* M.-T. Zhang* _____

Iron-Catalyzed Water Oxidation: O–O Bond Formation via Intramolecular Oxo– Oxo Interaction



Three binuclear Fe complexes are tested as molecular water oxidation catalysts. O-O bond formation can be achieved via intramolecular oxo-oxo interaction rather than by water nucleophilic attack (WNA), and the catalytic performance can be effectively controlled by the framework of the ligand.

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