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Redox Active Ligand Assisted Multi-Electron Catalysis: A Case of Co^{III} Complex as Water Oxidation Catalyst

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ABSTRACT: Water oxidation is the key step in both natural and artificial photosynthesis to capture solar energy for fuel production. The design of highly efficient and stable molecular catalysts for water oxidation based on non-precious metals is still a great challenge. In this article, the electrocatalytic oxidation of water by $Na[(L^+)Co^{III}]$, where L is substituted tetraamido macrocyclic ligand (TAML), have been investigated in aqueous solution (pH 7.0). We found that $Na[(L^+)Co^{III}]$ is a stable and efficient homogenous catalyst for electrocatalytic water oxidation with 380 mV onset overpotential in 0.1 M phosphate buffer (pH 7.0). Both ligand- and metal-centered redox features are involved in the catalytic cycle. In this cycle, $Na[(L^+)Co^{III}]$ was first oxidized to $[(L^{2^-})Co^{III}OH]$ via ligand-centered PCET process in the presence of water. After further losing an electron and a proton, the resting state, $[(L^2)Co^{III}OH]$, was converted to $[(L^{2^-})Co^{IV}=O]$. DFT calculations at the B3LYP-D3(BJ)/6-311++G(2df,2p)//B3LYP/6-31+G(d,p) level of theory confirmed the proposed catalytic cycle. According to both experimental and DFT results, phosphate-assisted water nucleophilic attack (WNA) to $[(L^{2^-})Co^{IV}=O]$ played a key role in O-O bond formation.

INTRODUCTION

Solar-to-fuel conversion chemistry is a highly active field in chemistry and material science due to the rising global energy demands and climate changes.¹⁻⁴ Inspired by nature,⁵⁻⁷ artificial photosynthesis, where solar energy is employed to split H₂O into O₂ and H₂, is deemed to be an attractive way to convert solar energy into fuels.⁸⁻¹⁴ Water oxidation $(2H_2O \rightarrow O_2 + 4e^{-} + 4H^{+})$, which provides the necessary reducing equivalents for both hydrogen evolution and CO₂ reduction, remains a bottleneck for solar-powered water splitting.^{11,15,16}Numerous molecular catalysts for water oxidation have been described,¹⁷⁻²⁰ including robust and highly active ones that based on second- and third-row transition metals, such as Ru²¹⁻³⁷ and Ir³⁸⁻⁴². In contrast, the development of molecular water oxidation catalysts (WOCs) based on earthabundant first-row transition metals that could operate under mild conditions (neutral pH) remains a challenge.^{18,43} Although examples based on Mn,⁴⁴⁻⁴⁸ Fe,⁴⁹⁻⁵³ Co,⁵⁴⁻⁶³ Ni^{64,65} and Cu⁶⁶⁻⁷² have been reported, most of these catalysts require a formal high oxidation state, such as Co(IV),⁷³ Fe(V)^{74,75}, Fe(VI),^{76,77} even Cu(IV)⁶⁸ to drive water oxidation. This led to relative liable catalytic systems and strong dependence on the reaction conditions such as pH and type of buffer and oxidant, compared to Ru based catalysts.⁴³ Therefore, the rational design of robust and efficient molecular water oxidation catalysts based on earthabundant first-row transition metals needs further exploration.

The intrinsic challenge of water oxidation catalysis is due to the multielectron catalytic process, which involved four steps of accumulative electron transfer.^{78,79} This requires the catalyst to reach a high formal oxidation state, and thus increase the difficulty of keeping the catalyst live and homogenous for a long time. In photosystem II (PSII), a Mn₄Ca-cluster in the oxygen evolution complex disperses the charges at multiple metal sites to evade the charge accumulated on a single metal center and avoid reaching a high oxidation state.^{15,80,81} To avoid charge accumulation, on the other hand, redox ligands were extensively used in metalloenzymatic and organometallic multi-electron reactions owing to synergistic ligand effect on reaching a formal high oxidation state.^{82,83} The latter strategy shows the possibility of tuning the reactivity and stability of high oxidation state intermediates by using redoxactive ligand relative to metal center,^{84,85} particularly for single site catalysis. Although simple cobalt salts have been known to catalyze water oxidation since the 1980s,^{86,87} for example, the development of cobalt-based molecular WOCs was boosted after in-situ generated cobalt-based WOC (Co-Pi) was reported by Nocera and coworkers.⁸⁸ A series of cobalt complexes with different kinds of ligands such as corrole, polypyridine, salen, and porphyrin were applied for electro- or photo-catalyzed water oxidation.⁵⁴⁻⁶³ However, a challenge for Cobased homogeneous catalyst development is the intrinsic instability of the high oxidation state intermediate from which the ligand easily liberated and CoO_x formed.⁸⁹⁻⁹²



Figure 1. (a) Structure of the $[(L_{1.3}^+)Co^{III}]^-$ catalysts, where Na⁺ is the countercation; (b) Structure of the $[(L^+)Co^{III}]^-$, where Na⁺ is the counter-cation; (c) ORTEP representation of Na $[(L_1^+)Co^{III}]$ (ellipsoids were drawn at 30% probability). Selected bond distance (Å) and angle (°): Co-N1 1.820(2), Co-N2 1.820(2), Co-N3 1.836(2), Co-N4 1.836(2), N1-Co-N2 85.8(1), N1-Co-N3 86.5(1), N3-Co-N4 101.2(1); (d) ORTEP representation of Na $[(L_4^+)Co^{III}]$ (ellipsoids were drawn at 30% probability). Selected bond distance (Å) and angle (°):Co-N1 1.832(4), Co-N2 1.859(4), Co-N3 1.811(4), Co-N4 1.810(4), N1-Co-N4 87.3(2), N1-Co-N2 99.6(2), N3-Co-N4 86.2 (2), N2-Co-N3 86.7 (2). Full crystallographic details are available in the Supporting Information.

In this contribution, we report a family of cobalt-based water oxidation catalysts supported by TAML ligands, where redox-active functionalities are incorporated at equatorial positions. These cobalt catalysts are capable of homogeneously electrocatalyzing water oxidation at pH 7, where the redox ligand facilitates the multi-electron catalysis by promoting synergistic accumulative electron-proton transfer. This feature further illustrated that the ligand-centered redox process was equally important to catalytic metal center for rational design of molecular catalyst for water oxidation.

RESULTS AND DISCUSSION

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Redox-active ligands have long been recognized not only for the intriguing electronic structure of the resulting metal complexes but also for their role as electron reservoirs.83 o-Diphenylenedicarboxamido(bpb2-) is a classic example of redox-active ligand. Scheme 1 shows the three possible redox forms of this ligand with o-diphenylenedicarboxamido (bpb²⁻) as its most reduced form, and o-dicarboxamido-semiquinonate (bpb⁻) and o-benzoquinonedicarboxamido (bpb⁰) as intermediate and the most oxidized form, respectively.93-95 Tetraamido macrocyclic ligand (TAML), developed by Collins and coworkers, is a derivative of bpb2- ligand and is capable of stabilizing unusual formal high valent metal ions such as Co(IV) and Fe(V), which were usually proposed as key intermediate for water oxidation.^{49,75,96-99} Inspired by these pioneer work, as well as the redox properties of bpb²⁻ type ligand, we selected a series complexes, $Na[(L_{1.3}^{4+})Co^{III}]$ (Figure 1), as model complexes to investigate the metal-ligand cooperation in water oxidation. Since both metal and ligand have variable oxidation state, in principle, the catalyst is more likely to reach a higher formal oxidation state and thus facilitate the water oxidation. To clearly understand the importance of redox ligand, an analog with non-redox ligand, $Na[(L_4^{4-})Co^{III}]$ was selected as reference. Based on the above considerations, we have conducted the investigations presented as follows.

Scheme 1



Synthesis and Characterization of Na[(L⁺)Co^{III}]. Ligands (H₄L₁₋₄) listed in Figure 1 were synthesized through a modified literature procedure (the details were listed in SI).^{100,101} The ligands were deprotonated by NaHMDS and coordinated to CoCl₂ in THF under an argon atmosphere. The desired Co(III) complexes were obtained under air exposure.¹⁰⁰ The cobalt complexes are negatively charged and the counter-cation is Na⁺. X-ray crystallography (Figure 1) showed that Co(III) in solid state is in a square-planar coordination sphere comprised of four deprotonated N atoms of the ligand moiety, which is similar to the reported structure.¹⁰⁰ These complexes were characterized by ESI-MS and ¹H NMR. Typical paramagnetically shifted ¹H NMR spectra of square planar Co^{III} (S = 1) systems (Figure S1-S7) were observed for these complexes. DFT calculation showed these Co(III) complexes still adopt four coordination without an aqua in water, and the details will be discussed below.

Electrochemical Properties of Na[(L^+)**Co**^{III}] **in water at pH 7.0**. *Cyclic Voltammograms.* The electrochemical behaviors of Na[(L^+)Co^{III}] were investigated in 0.1 M phosphate buffer solution at pH 7.0, and the results are listed in Table 1 and illustrated in Figure 2 and Figures S8-S9. Figure 2 shows a typical CV *i*-*E* response of Na[(L_1^+)Co^{III}] and its variation with scan rates (*i* vs v^{1/2}). Two irreversible oxidation processes were observed at $E_{p,a}$ = 1.001 V and 1.476 V (vs NHE), respectively.

The latter wave has a greatly enhanced underlying current compared to the background (Figure 2a, red line). The $i \sim v^{1/2}$ graph in Figure 2b showed that the first wave with $E_{p,a} = 1.00$ V is independent on $v^{1/2}$ and the second wave with $E_{p,a} = 1.48$ V is proportional to $v^{1/2}$, indicating that the first wave relates to a diffusion-controlled process and the second wave relates to a catalytic process. The onset potential for this catalytic process appears at ~1.20 V *vs* NHE. In contrast to Na[(L_{1.3}⁺)Co^{III}], the complex with the non-redox ligand, Na[(L₄⁺)Co^{III}], only displayed a non-catalytic irreversible wave at 1.308 V *vs* NHE (Figure 2a, blue dash line).

Confirmation of Oxygen Evolution. Oxygen evolution was confirmed by bulk electrolysis at +1.40 V (*versus* Ag/AgCl) on an ITO electrode with a large surface area (1 cm²), employing 1 mM Na[(L₁⁴)Co^{III}] in phosphate buffer (pH 7.0). The oxygen formed in the solution was measured using a calibrated Ocean Optics FOXY probe (Figure 3). The oxygen generated at the applied potential in the absence of catalyst was negligibly small, while with 1 mM Na[(L₁⁴)Co^{III}] added, the catalytic current was sustained at a stable current density of 0.25 mA/cm² (Figure S10). The dissolved O₂ in the solution phase increased from 65 to 256 μ M in 1 h with a Faraday efficiency over 90% for the O₂ evolution, indicating that the catalytic wave observed in Figure 2a is a water oxidation process with an onset overpotential of 380 mV.



Figure 2. (a) CVs of 0.5 mM Na[$(L_1^+)Co^{III}$ (red line), 0.5 mM Na[$(L_4^+)Co^{III}$ (blue dash line) and blank (black line) at glassy carbon (GC) electrode at 50 mV/s in 0.1 M pH = 7.0 phosphate buffer; (b) Normalized CVs of 0.5 mM Na[$(L_1^+)Co^{III}$] in 0.1 M pH = 7.0 phosphate buffer at GC at different scan rates. *Proof for Homogeneous Catalysis.* To distinguish homogeneous and heterogeneous WOCs has received particular concern respect to the

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challenge of molecular catalyst stability. Given the fact that the robust and effective heterogeneous catalyst, CoOx, could be easily formed during catalysis from simple aqueous Co²⁺ or molecular pre-catalyst, we thus investigated stability of Na[(L⁴)Co^{III}] WOCs under electrocatalytic conditions. Over multiple CVs at GC and ITO electrode, there were insignificant changes in peak currents or wave shapes. Electrodes after multiple CVs gave no catalytic response in a fresh, cobalt-catalystfree electrolyte at pH 7.0 (Figure S11-S12). XPS result showed no signal of CoO_x formed on the ITO electrode after bulk electrolysis (Figure S13); SEM of ITO surface topography also showed no cobalt oxide precipitated during electrolysis (Figure S14). The electrochemical behaviors of $Na[(L^4)Co^{III}]$ strongly rely on the ligand (Figure S8), which differs from the previously reported Co-Pi catalyst,⁸⁸ which excludes the self-healing cobalt oxide catalysis. Taking these observations into account, the results provide strong evidences for the key role of structurally intact $Na[(L^4)Co^{III}]$ in the electrocatalytic cycle and a homogeneous catalysis process proceeded under the conditions used here, despite the difficulty to definitively exclude a colloid material.



Figure 3. Oxygen evolution during bulk electrolysis at the applied potential 1.40 V vs Ag/AgCl. Conditions: 1 mM $Na[(L_1^4)Co^{III}]$; 0.1 M phosphate buffer solution (PBS) at pH 7.0; ITO electrode (1 cm²);



Figure 4. Pourbaix diagram of Na[$(L_1^+)Co^{III}$] in 0.1 M phosphate buffer solutions (black and blue dots represent the potentials for the first and second wave in CV, respectively). All data were determined by differential potential voltammetry method using a glassy carbon electrode as the working electrode.

Ligand-Centered Proton-Coupled Electron Transfer. The electrochemical behaviors of $Na[(L_1^+)Co^{111}]$ at full pH range from 5 to 11 were carried out in 0.1 M phosphate buffer solutions (Figure S15), and the resulted *E* - pH diagram was shown in Figure 4. As shown in the CV graph (Figure 2), there are two irreversible oxidation waves at $E_{p,a}$ = 1.00 and 1.48 V (*vs* NHE) at pH 7.0, respectively. The first irreversible oxidation wave is pH-dependent from pH = 5 to 9 with a slope of 30 mV/pH, and the slope became 59 mV at pH > 9.0. Three lines of evidences indicate this oxidation wave proceeds as a ligand-centered proton-coupled oxidation of Na[(L₁⁴⁻)Co^{III}] to[(L₁²⁻)Co^{III}OH] as showed in Eq.1-2. At the 5 < pH < 9 range, it proceeded as shown in Eq. 1,

$$(L^{4-})Co^{III} + H_2O \rightarrow (L^{2-})Co^{III}OH + 2e^- + H^+$$
 (1)
and at pH > 9, the oxidation wave occurred as shown in Eq. 2
 $(L^{4-})Co^{III} + H_2O \rightarrow (L^{2-})Co^{III}O^- + 2e^- + 2H^+$ (2)



Figure 5. Cyclic voltammograms of 0.5 mM $[(L_1^+)Co^{III}]^-$ (black), $[(L_2^+)Co^{III}]^-$ (red), $[(L_3^+)Co^{III}]^-$ (blue), and the reference compound with non-redox ligand $[(L_4^+)Co^{III}]^-$ (green) in degassed anhydrous CH₃CN solution (with 0.1 M TBA·PF₆ as electrolyte). Boron-doped diamond (BDD) electrode was used as working electrode and the scan rate is 50 mV/s.

Table 1. $E_{1/2}$ values for four Na[(L⁴⁻)Co^{III}] complexes in acetonitrile and phosphate buffer (pH 7.0)

Compd.	$CH_3CN (V vs Fc^{+/0})^a$			Water (V vs NHE) ^b	
	$Co^{III/II}$	L ^{4-/3-}	Co ^{IV/III -}	L ^{4-/2-}	Co ^{IV/III}
$Na[(L_1^4)Co^{III}]$	-1.17	0.49	0.89	1.00	1.476
$Na[(L_2^4)Co^{III}]$	-1.06	0.64	0.94	1.05	1.478
$Na[(L_3^4)Co^{III}]$	-1.23	0.34	0.84	0.90	1.474
$Na[(L_4^4)Co^{III}]$	-1.46	-	0.80	-	1.308

^a The CV shape is strongly dependent on the water content of the electrolyte solution. The solution was carefully degassed and its water content was kept less than 10 ppm during the measurement. ^b0.1 M phosphate buffer (pH 7.0) was used as electrolyte solution, the potentials were determined by differential pulse voltammetry (DPV) method.

First, the ligand is easier to be oxidized than the Co^{III} center of Na[(L₁. $_{3}^{4}$)Co^{III}] in acetonitrile (ligand-centered oxidation). CVs of Na[(L₁. $_{3}^{4}$)Co^{III}] complexes employed in this study displayed a reversible Co^{III/II} reduction wave at -1.06 to -1.23 V, two reversible one electron transfer oxidation waves at 0.34 to 0.64 V and 0.84 to 0.94 V (*versus* Fc^{+/0}) in CH₃CN (Figure 5), respectively. These two waves are in agreement with the reported *o*-diphenylenedicarboxamido (bpb²⁻) ligated Co^{III} complex.⁹⁶ The electrochemical behavior of the complex with non-redox ligand Na[(L₄⁴⁺)Co^{III}] (Figure 5) displayed only two waves at -1.46 V and 0.80 V, but without a reversible wave at 0.34 to 0.64 V. Since the electrochemically generated monooxidized species, namely [(L_{1.3}³⁻)Co^{III}], are stable in acetonitrile, the UV-*vis* spectra was record-

ed. $[(L_1^{3-})Co^{III}]$ species displayed intense new absorptions in visible and near-infrared regions (596 and 746 nm) that are characteristic of (imino)semiquinonato radical (bpb⁻)⁹⁶ (Figure S16). The EPR spectrum of this electrochemically generated monooxidized species in acetonitrile has an isotropic character with a *g* value of 1.997 (Figure 6), indicating that the oxidation of $[(L_{1\cdot3}^+) Co^{III}]^-$ is ligand-centered, with the formation of the corresponding (imino)semiquinonato organic radical (bpb⁻). These results indicated that the reversible wave at 0.34 to 0.64 V(*versus* Fc^{+/0}), which is strongly dependent on the substituents on the ligand, should be ascribed to the ligand-centered oxidation, while the wave at 0.84 to 0.94 V (*versus* Fc^{+/0}) should be attributed to the oxidation of Co^{III}.

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Second, the electrochemical behavior of the cobalt complex with the non-redox ligand, $Na[(L_4^4)Co^{III}]$ (Figure 6), shows that the first irreversible oxidation wave around 1.0 V vs NHE of Na[(L1.3+)Co^{III}] would be a ligand-centered proton-coupled electron transfer process. Interestingly, the electrochemical behavior of $Na[(L_1^4)Co^{III}]$ in CH₃CN/H₂O was quite different. Upon gradually addition of water to acetonitrile solution of $Na[(L_1^{4-})Co^{III}]$, the wave of ligand-centered oxidation at 0.49 V (versus $Fc^{\scriptscriptstyle +/0})$ became irreversible and the anodic current increased at 0.96 V, indicating an electrocatalytic oxidation behavior (Figure S17-S19). Due to the existence of H₂O, the electrochemical behavior in buffer is different from the successive single electron and reversible redox behavior of $[(L_1^4)Co^{III}]^2/[(L_1^{3-})Co^{III}]$ and $[(L_1^{3-})Co^{IV}]/[(L_1^{3-})Co^{III}]^+$ displayed in acetonitrile. Upon oxidation of $[(L_1^{4-})Co^{III}]$ in aqueous solution, the H₂O molecular coordinates to the Co center and the second proton-coupled electron transfer occurs simultaneously. The net result, formation of $[(L_1^{2-})Co^{III}-OH]$, is equivalent to a combined "formal" $(2e^{-} + H^{+})$ oxidation and hydroxide binding. Figure 6b shows a typical electrochemical behavior of both $Na[(L_{1^{4+}})Co^{III}]$ and $Na[(L_{4^{4+}})Co^{III}]$. The former compound, which has a redox-active ligand (L_1) , displayed the an irreversible oxidation wave around 1.0 V vs NHE, while for the latter with the non redoxactive ligand (L₄), there is no electrochemical response around 1.0 V vs NHE. This result, together with the E-pH relationship, supports that the first irreversible oxidation wave around 1.0 V vs NHE should be ascribed to the ligand-centered PCET oxidation of Na[(L1-34-)CoIII] with the help of H₂O.



Figure 6. (a) EPR spectrum of $Na[(L_1^+)Co^{III}]$ electrolyzed under the potential of 0.6 V vs Fc^{+/0} at 295 K. (b) Electrochemical behaviors of $Na[(L_1^+)Co^{III}]$ (red line) and $Na[(L_4^+)Co^{III}]$ (blue line) in pH 7.0 phosphate buffer (0.1M) compared with blank (black line) indicating the oxidative wave at 0.9 V vs NHE belongs to the ligand-centered PCET oxidation.

Third, as shown by ESI-HRMS, the electrolysis at 1.2 V vs NHE caused the disappearance of the $[(L_1^+)Co^{III}]^-$ peak (m/z = 429.0792, Figure S1) and the appearance of a new peak at m/z = 468.0886, which was designated as $\{[(L_1^{2-})Co^{III}-OH]+H_2O-H^+\}^-$ (Figure S20). When $[(L_3^+)Co^{III}]^-$ was treated with bulk electrolysis at 1.2 V vs NHE, the $\{[(L_3^{2-})Co^{III}-OH]+H_2O-H^+\}^-$ peak (m/z = 531.0259, Figure S21) was

also observed. Additionally, the electrolysis at 1.2 V vs NHE resulted in the oxidation of $[(L_1^4)Co^{III}]$ to $[(L_1^{2})Co^{III}-OH]$, leading to a loss of intensity of the LMCT band at 230 and 265 nm and increasement of the MLCT band at 338 and 412 nm, as well as the bleach at 600 nm. These are probably due to the changes of *d*-*d* transition caused by the coordination environment transformed from square to quadrangular pyramid (Figure S22). X-ray photoelectron spectra (Figure 7) of $[(L_1^4)]$) Co^{III} and the [(L_1^2) Co^{III} -OH] sample prepared by bulk electrolysis at 1.2 V vs NHE display very similar binding energies (780.3 eV for Co $2p_{3/2}$ and 795.5 eV for Co $2p_{1/2}$ of $[(L_1^{4-})Co^{111}]$; 780.8 eV for Co $2p_{3/2}$ and 796.3 eV for Co $2p_{1/2}$ of [(L_1^{2-})Co^{III}-OH], the weak yellow satellite peaks in both cobalt complexes' Co 2p region probably were the shakeup lines of Co(III))¹⁰²⁻¹⁰⁴ consistent with Co(III) oxidation state,¹⁰⁵⁻¹⁰⁷ indicating that the oxidation process at 1.2 V vs NHE happened on the ligand rather than Co(III) center. In contrast, the O 1s region of the XPS spectrum of [(L12)Co^{III}-OH] has an additional peak at 532.0 eV compared with the spectrum of $[(L_1^4)Co^{III}]^-$ (530.9 and 532.2 eV for $[(L_1^4)Co^{III}]$; 531.2, 532.0, and 532.6 eV for $[(L_1^{2-})Co^{III}-OH])$. The binding energy peak at 532.0 eV is consistent with an OH group binding on the Co(III).¹⁰⁸⁻¹¹¹ This matches well with the ligand-centered PCET 2e⁻ oxidation involving a H₂O and [(L²⁻)Co^{III}-OH] is the resulted resting state for water oxidation catalysis. From these data, it is clear that the ligand has undergone a PCET oxidation with H2O involved in the process (Eq. 1 and Eq. 2).



Figure 7. (a) Co 2p region of the XPS spectrum of Na[$(L_1^+)Co^{III}$], (b) O 1s region of XPS spectrum of Na[$(L_1^+)Co^{III}$], (c) Co 2p region of the XPS spectrum of [$(L_1^{-2})Co^{III}$ (OH)] synthesized by bulk electrolysis, (d) O 1s region of the XPS spectrum of [$(L_1^{-2})Co^{III}$ (OH)] obtained by bulk electrolysis.

Water Oxidation Kinetics and Mechanistic Analysis. The second irreversible oxidation wave (Figure 2), which is an electrocatalytic water oxidation process also displays pH dependence with a slope of 52 mV/pH at 5 < pH < 9 range, indicative of a PCET oxidation of $[(L^{2-})Co^{II}-OH]$ (Eq. 3).

$$(L^{2-})Co^{III}OH \rightarrow (L^{2-})Co^{III} - O \cdot + e^{-} + H^{+}$$
 (3)

At pH>9, The second irreversible oxidation wave (Figure 2) displays pH independence since $[(L^{2-})Co^{III}-OH](pK_a = 9.3)$ was deprotonated, indicative of a single electron oxidation of $[(L^{2-})Co^{III}-O^{-}]$ (Eq. 4).

$$(L^{2-})Co^{III}O^{-} \to (L^{2-})Co^{III} - O^{\cdot} + e^{-}$$
 (4)

The resulting intermediate, $[(L^{2-})Co^{IV}=O]$ or $[(L^{2-})Co^{III}-O^{-}]$, might react with water to form the O-O bond and enable the catalytic cycle of water oxidation (Eq. 5).

$$(L^{2-})Co^{IV} = 0 + H_2 0 \rightarrow (L^{4-})Co^{III} + 0_2 \uparrow + e^- + 2H^+$$
 (5)



Figure 8. (a) CVs of different concentrations of Na[(L_1^+)Co^{III}] in 0.1 M PBS buffer at pH = 7.0 (insert: linear regression of i_{cat} vs catalyst concentration, [Cat.].); (b) Plot of linear regression of i_{cat}/i_d vs $v^{1/2}$.

Kinetic Analysis. The catalytic current is linearly dependent on the bulk concentrations of catalyst (Figure 8a), thus the peak current of this catalytic process should obey the relationship displayed in Eq. 6,¹¹² where A is the electrode surface area, *F* is Faraday constants, *i*_d is the peak current, *i*_{cat} is the peak current of the catalytic wave, [Co] is the bulk concentration of catalyst, D_{Co} is the diffusion coefficient of the catalyst, and $n_{cat} = 4$ is the number of electrons transferred in each catalytic cycle.

$$i_{cat} = n_{cat} FA[Co](k_{cat}D_{Co})^{\frac{1}{2}}$$
 (6)

Scan rate normalized CVs (i/\sqrt{v}) at different scan rates shows that the first oxidation wave is related to an irreversible diffusion limited proton-coupled electron transfer (PCET) at the electrode. The peak current (*i*_d) varies linearly with \sqrt{v} , which is in consistent with the Randles-Svecik equation in Eq. 7,¹¹² where $n_d = 2$ is the number of of electrons transferred in this diffusion controlled process, $\alpha = 0.5$ is the transfer coefficient of the catalyst.

$$i_d = 0.496 n_d \alpha^{1/2} FA[Co] \left(\frac{n_d F v D_{Co}}{RT}\right)^{\frac{1}{2}}$$
(7)

By dividing Eq. 6 by Eq. 7, a relationship between i_{cat} and i_d could be obtained (Eq. 8) and the rate constants for water oxidation could be evaluated using this equation.

$$\frac{i_{cat}}{i_d} = 0.359 \frac{n_{cat}}{n_d^{3/2}} \sqrt{k_{cat}/\alpha v}$$
(8)

Figure 8b showed the expected linear variation of i_{cat}/i_d with \sqrt{v} , and the k_{cat} , calculated from the slope, was 7.53 s⁻¹, 7.58 s⁻¹ and 8.81 s⁻¹ for $[(L_1^+)Co^{III}]$, $[(L_2^+)Co^{III}]$, and $[(L_3^+)Co^{III}]$, respectively (Figure 8, S23-S29). The catalytic rates of these catalysts compare well with those reported k_{cat} around 1 s⁻¹ for the single site and polynuclear cobalt-based WOCs.⁵⁶⁻⁵⁸ Notably, no catalytic water oxidation behavior was observed for the complex with the non redox-active ligand, $[(L_4^+)Co^{III}]$, indicating that the redox-active ligand plays a critical role in this multi-electron catalytic cycle.

Proposed mechanism. The catalytic peak current for water oxidation i_{cat} varies linearly with the concentration of catalyst, Na[(L₁₋₃⁴⁻)Co^{III}], consistent with single-site cobalt catalysis (Figure 8a, S24, S27). CV experiments were also performed in D_2O (pD = 7.0) phosphate buffer (Figure S30). Analysis of these data gave a kinetic isotope effect (KIE = $k_{\rm H2O}/k_{\rm D2O}$) of 2.0. As similar to the oxidation of water by Ru^V=O, this kinetic isotope effect might be attributed to atom-proton transfer (APT) with O-O bond formation concerted with proton transfer to a proton acceptor, such as base form of buffer.^{113,114} The electrochemical behaviors at different buffer concentrations were carried out at an adjusted ionic strength I = 0.462 M by NaClO₄ (Figures S31-S32) and the dependence of $(i_{cat}/i_d)^2$ on phosphate concentrations (0 ~ 0.2 M) indicated the buffer anion as proton acceptor could contribute to rate limiting water nucleophilic attack of Co^{IV}=O. In terms of the available experimental results, water oxidation mechanism in Scheme 2 was proposed, in which O-O bond formation step is analogous to the scheme proposed earlier for Ru polypyridyl catalysts.^{26,113,114} In this catalytic cycle, the resting state, $[(L_1^{2-})Co^{III}-OH]$ was formed by a ligand-centered (2e⁻ + H⁺) involved PCET oxidation, and a further PCET oxidation generated the catalytically active $[(L_1^2)Co^{IV}=O]$, which reacts with water by rate limiting O-O bond formation step to give an intermediate peroxide that could be further oxidized to release oxygen and close the cycle.



Scheme 2. Proposed mechanism of $Na[(L_1^+)Co^{III}]$ in phosphate buffer solutions (pH = 7.0)



Figure 9. Energy diagram (ΔG_{298K} in kcal·mol⁻¹) for water oxidation catalyzed by Na[(L₁⁴)Co^{III}], calculated at the B3LYP-D3(BJ)/6-311++G(2df,2p)//B3LYP/6-31+G(d,p) level. The reference potential of 1.40 V vs NHE is used to setup the thermodynamics. The Gibbs free energies and the potentials for redox couples under pH 7 are reported.

DFT calculation. To disclose more details of the water oxidation catalytic cycle, in particular the oxygen-oxygen bond formation event, density functional theory calculation was performed at the B3LYP-D3(BJ)/6-311++G(2df,2p)//B3LYP/6-31+G(d,p) level. For the intermediates and the transition states, the solvation effect in water was taken into account by applying the SMD model during single-point energy calculation based on the gas-phase optimized structures. For the H₂O molecule, proton, and sodium cation, the experimental solvation free energies in water were used.

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The model WOC employed in the DFT calculation is the triplet state complex $Na[(L_1^4)Co^{III}]$ (Figure 9). In aqueous solution, $Na[(L_1^4)Co^{III}]$)Co^{III} combines one H₂O molecule and undergoes PCET ($H^+ + 2e^-$) to give a triplet complex $[(L_1^{2-})Co^{III}-OH]$, in which a hydroxyl group coordinates at the top of the complex and the redox-active tetraamido macrocyclic ligand was oxidized (L⁴⁻ to L²⁻). The oxidation of the TAML moiety is clearly indicated by the changes in structural parameters: in the starting complex $Na[(L_1^4)Co^{III}]$, the C-C bond length of the benzene ring is evenly distributed (around 1.40 Å), and the Naryl ring bond lengths are ca. 1.41 Å; in the complex $[(L_1^{2-})Co^{III}-$ OH] after a PCET $(H^+ + 2e^{-})$, the C-C bonds in the former benzene ring are elongated and shortened alternately (1.42 and 1.38 Å, respectively), and the two N-aryl ring bonds shortened to 1.36 Å. This is in accordance with the structural change in the oxidation of an odiphenylenedicarboxamido ligand to its benzoquinonedicarboxamido form. The calculated natural bond orbital (NBO) charge distributions of $Na[(L_1^{4-})Co^{III}]$ and $[(L_1^{2-})Co^{III}-OH]$ also support the ligandcentered PCET, because the charge on the ligand moiety changed from -1.885 to -0.482 during this process. The complex $[(L_1^{2-})Co^{III}-OH]$ is

further oxidized through another PCET process to produce the proposed complex $[(L_1^{2\cdot})Co^{IV}=O] \leftrightarrow [(L_1^{2\cdot})Co^{III}-O\cdot]$. Analysis of the calculated structure revealed that, both the oxo moiety and the cobalt center bear significant spin densities. Therefore the structure of the complex is better described as $[(L_1^{2\cdot})Co^{III}-O\cdot]$ (see the Supporting Information for details).

The oxidation potentials of these two PCET steps at pH 7 were calculated to be 0.91 and 1.32 V vs NHE, respectively, in agreement with the experimental CV diagram for Na[$(L_1^+)Co^{III}$] (Figure 2a), in which two oxidation waves were found at 1.00 and 1.48 V vs NHE. This also accounts for the experimental Pourbaix diagram (Figure 4), which indicates a H⁺ + 2^e process for the first wave, and a H⁺ + e⁻ process for the second wave.

The crucial oxygen-oxygen bond formation step follows a water nucleophilic attack (WNA) mechanism, in which the assistance of the buffer anion plays an important role. First, $[(L_1^{2-})Co^{III}-O\cdot]$ binds with NaH₂PO₄ and a H₂O molecule to give intermediate Intl, in which Na⁺ attached to one amide carbonyl group and the phosphate moiety, together with the H₂O, complexed with Na⁺. This process is exergonic by 4.4 kcal/mol. Then the H₂PO₄ anion assisted the nucleophilic attack of the H₂O molecule at the oxo group of $[(L_1^{2-})Co^{III}-O\cdot]$: in the WNA transition state **TS**, the $H_2PO_4^-$ anion binds to the oxo group by hydrogen bonding interaction (O.-H distance: 1.74 Å), and it facilitates the attack of the oxygen in H₂O to the oxo group (O...O distance: 1.83 Å) by abstracting a proton from H₂O (Figure 9). The WNA process has an activation free energy of 16.8 kcal/mol, and it turns out to be the rate-limiting step in the catalytic cycle.¹¹⁵ An alternative WNA pathway, which follows the established WNA model for the Fe-TAML complexes involving multiple H₂O molecules, was

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also calculated.^{76,77} It was found that, association of four H₂O molecules with $[(L_1^{2})Co^{III}-O^{\cdot}]$ is endogonic by 19.2 kcal/mol. In the WNA transition state TS', these water molecules form a hydrogen bonding network and the nucleophilic attack of one H2O to the oxo group (O…O distance: 1.78 Å) is facilitated by proton abstraction from another H₂O molecule. However, this pathway has an overall activation free energy of 42.8 kcal/mol (from Int1), much higher than that of the dihydrophosphate-assisted pathway. The significant influence of H₂PO₄⁻ on the WNA process revealed by DFT calculation 10 is in good agreement with the observed buffer effect. 11 Both WNA pathways affords the quartet hydroperoxo cobalt(II)

complex, $[(L_1^{2})Co^{II}-OOH]$. This species is oxidized to the superoxo $cobalt(III) complex [(L_1^4)Co^{III} O_2] through a PCET process, with a$ calculated redox potential of 1.07 V at pH 7. Therefore, under the applied potential this PCET process could occur directly. Finally, complex $[(L_1^4)Co^{III} \cdot O_2]$ releases oxygen molecule and combines with Na⁺ to regenerate the WOC $Na[(L_1^4)Co^{III}]$, which is dramatically exergonic by 25.3 kcal/mol. The overall driving force for water oxidation under the reference potential (1.4 V vs NHE) is calculated to be -54.8 kcal/mol in terms of Gibbs free energy, which is in good agreement with the theoretical value (-53.8 kcal/mol).

The DFT study supports the proposed mechanism for water oxidation by the Co-TAML complexes, and reveals the molecular details in the oxygen-oxygen bond formation event, in which the phosphateassisted water nucleophilic attack played a key role. The experimental observations, including the electrochemical properties, the water oxidation kinetics, and the buffer effect, could be rationalized by this mechanism.

CONCLUSIONS

In summary, we report highly efficient electrocatalytic water oxidation in neutral aqueous solution (pH 7.0) by stable Co(III) complexes bearing redox active ligands. In addition, as CoO_x is known to be highly active for water oxidation, Co(III) complex was conformed as molecular catalyst under the working conditions. The catalytic cycle was examined in details by electrochemical method in combination with DFT calculation. Upon the working potential increased, the Na[(L4-)Co(III)] complex is firstly oxidized to $[(L^{2})Co^{III}-OH]$ via ligandcentered proton coupled electron transfer $(2e^{-} + H^{+})$ in the presence of water. The resulted resting state, $[(L^{2-})Co^{III}-OH]$, was further oxidized to $[(L^{2})Co^{IV}=O]$ which could react with water to form O-O bond with the help of buffer anion. These results indicate that the interplay of ligand- and metal-centered redox activity is benefit for water oxidation catalysts. We will focus our attention on developing new catalysts based on redox ligand and further understanding the structurefunction-reactivity relationship of these redox ligands in water oxidation catalysis.

ASSOCIATED CONTENT

Supporting Information. Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interests. We would like to dedicate this work to Prof. Jin-Pei Cheng on the occasion of his 70th birthday.

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Other WNA pathways assisted by different anions were also modeled and d in terms of activation Gibbs free energy. See the Supporting Information for

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TOC Graphic:

