A Water Nucleophilic Attack Mechanism for the Cu(pyalk) Water Oxidation Catalyst


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A Water-Nucleophilic Attack Mechanism for the 

$\text{Cu}^{\text{II}}(\text{pyalk})_2$ Water-Oxidation Catalyst

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**ABSTRACT:** We investigate the mechanism of water oxidation catalyzed by the $\text{Cu}^{\text{II}}(\text{pyalk})_2$ complex, combining density functional theory with experimental measurements of turnover frequencies, UV-visible spectra, H/D kinetic isotope effects, electrochemical analysis, and synthesis of a derivative complex. We find that, only in the cis form, $\text{Cu}^{\text{II}}(\text{pyalk})_2$ converts water to dioxygen. In a series of alternating chemical and electrochemical steps, the catalyst is activated to form a metal oxyl radical species that undergoes a water-nucleophilic attack defining the rate-limiting step of the reaction. The experimental H/D KIE (3.4) is in agreement with the calculated value (3.7), shown to be determined by deprotonation of the substrate nucleophile upon O–O bond formation. The reported mechanistic findings are particularly valuable for the rational design of complexes inspired by $\text{Cu}^{\text{II}}(\text{pyalk})_2$.

**KEYWORDS**

water oxidation, catalysis, copper, water nucleophilic attack, density functional theory, electrocatalysis
# INTRODUCTION

Catalytic water oxidation is a critical bottleneck in the generation of solar fuels, a challenging reaction that requires powerful and robust catalysts. Transition metal catalysts require ligands that can stabilize high oxidation states and, at the same time, resist degradation under the harsh oxidative conditions. We have found that the ligand 2-(2′-pyridyl)-2-propanoate (pyalk) is an exceptionally apt chelate that fulfills these requirements, forming Ir-based water-oxidation catalysts (WOCs) that can be activated either chemically or electrochemically. Through collaborative theoretical and experimental efforts, the solution structures of Ir-pyalk water-oxidation catalysts have been determined. Recent efforts have focused on developing WOCs based on Earth-abundant metal centers, including manganese and copper. However, the underlying reaction mechanisms of these new catalysts have yet to be established. In fact, little is known about the mechanism of electrocatalytic water oxidation by copper complexes despite the first molecular Cu WOC being reported in 2012.

Three commonly proposed water-oxidation mechanisms for transition metal catalysts include the water-nucleophilic attack (WNA) on a metal oxyl-radical species, the interaction of two radical M—O• groups, and redox isomerization. Another possible mechanism, involving direct coupling to oxo bridges, is proposed by Siegbahn and co-workers for water oxidation in the Mn cluster of the oxygen evolving complex of Photosystem II, in synthetic Mn catalysts, and in a dinuclear copper complex. Additionally hydroperoxo intermediates have also been reported by Maseras, Llobet, and co-workers in what is termed “single electron transfer/water-nucleophilic attack”. Here, we explore the mechanism of the Cu(pyalk)_2 catalyst.
A recent study of dimeric copper WOCs has suggested that a dinuclear water-nucleophilic attack or a redox-isomerization pathway may play a major role in copper-based electrocatalytic water oxidation. Many copper WOCs have been shown to have first-order kinetics in copper over a wide concentration range, suggesting that a mononuclear pathway may be viable. Such a pathway could occur through a Cu(III)-oxyl radical intermediate, rather than a Cu(IV)-oxo intermediate, consistent with the “oxo wall” concept (no tetragonal terminal oxo species have been isolated for any transition metal from group 9 onwards). Such species have been suggested but never observed experimentally.

In this paper, we focus on elucidating the mechanism of the recently reported complex Cu(pyalk)$_2$ (1), found to be an active and robust electrocatalyst for water oxidation under basic conditions. We previously found that the catalyst has a TOF of 0.7 s$^{-1}$, at pH = 12.5, shows a first-order dependence on copper, and remains active for over 30 catalytic turnovers with minimal degradation. However, neither the active form of the catalyst nor the catalytic mechanism could be resolved. In this work, we find that the catalyst is active only in the cis isomer, 2 (Chart 1). Our proposed mechanism involves proton-coupled electron transfer (PCET) based on a water-nucleophilic attack onto a terminal oxyl radical species.

Chart 1. The structure of the proposed active form: cis Cu$^{II}$pyalk)$_2$, (2).

In this work, we investigate the catalytically active isomeric form and propose a plausible mechanism for a mononuclear catalyst. The resulting mechanism accounts for the multiple oxidation state transitions that are required for water oxidation, offering fundamental insights valuable for development of earth-abundant water-oxidation catalysts.
THEORETICAL METHODS

Calculations were based on unrestricted density functional theory (DFT) using the functional ωB97X-D\textsuperscript{20,21} which includes dispersion interactions, as implemented in Gaussian 09, Revision D.01.\textsuperscript{22} Comparisons to calculations based on B3LYP\textsuperscript{23} are included in the supporting information (SI). The ωB97X-D functional has been found to be quite useful for describing open-shell transition metal systems,\textsuperscript{24} water clusters\textsuperscript{25} and hydrogen bonds.\textsuperscript{26} The basis set used for geometry optimization, normal mode analysis (and calculations of free energy corrections\textsuperscript{27}), and time-dependent DFT (TDDFT) calculations, included the double zeta basis set def2-SVP\textsuperscript{28} for all elements but O, which was treated with 6-31+G(d,p),\textsuperscript{29,30} for the negative charges that reside on the anionic pyalk ligands, in particular, as recommended in the literature.\textsuperscript{31,32} Single-point energy calculations of the optimized structures and wavefunction stability checks (for the minima)\textsuperscript{33,34} were based on the triple-zeta basis set 6-311+G(2df,p) for all atoms.\textsuperscript{29,35-40} Calculations without the diffuse functions (def2-SVP for all atoms for the optimization and frequency calculations and def2-TZVP for all atoms in the single point calculations) were done as a test as discussed in Section S9.

The Cu(II) and Cu(III)-oxyl radical species are open-shell doublets with the former having the spin reside on the Cu and the latter having the spin reside on oxyl. Nevertheless, they do not to require corrections for spin contamination (SI, Section S2). Table S2 gives the spin densities used to confirm the oxidation states of various radical species. We tested the possibility of a high spin Cu(III) antiferromagnetically coupled to the oxyl radical and found this configuration instead optimized to one with a Cu(II) and a pyalk O having spin densities of 0.66 and 0.84, respectively, antiferromagnetically coupled to the oxyl radical with a spin density of -0.88. Because it was more energetically costly by 4.6 kcal/mol and suffered from significant spin
contamination, it was not considered further. Additionally, we tested other possible spin states for each species as indicated in Table S3, which were all found to be higher in energy.

Calculations of imaginary frequencies and intrinsic reaction coordinates (IRCs) (using local quadratic approximations (LQA)) were used to confirm the identity of the transition states. These are given in the SI in Section S5. Barrier heights are computed from the difference in free energies of the transition state and the minimum immediately before. The activation free energy for the overall reaction is taken as the activation free energy for water-nucleophilic attack (step V) as its transition state is the highest point on the computed potential energy surface and the minimum preceding it is the lowest point, considering the potentials applied, as recommend in the literature.

Theoretical UV-Vis spectra were generated using 30 singlet states, and a Gaussian broadening factor with full-width at half-maximum (FWHM) of 4839.33 cm\(^{-1}\) (0.6 eV) chosen for best comparison to experiment. The intensities of the theoretical spectra were scaled consistently. The integration grid for the DFT multielectron integrals was “ultrafine”, a pruned grid of 99 radial shells and 590 angular points for each shell. Structures were optimized to the rigorous “tight” criteria with a maximum step size of 0.000015 au, root-mean-square (RMS) step size of 0.000010 au, maximum force of 0.000060 au, and RMS force threshold of 0.000040 au.

Geometry optimizations of structures were undertaken within the dielectric continuum model, using the SMD\(^{51-54}\) solvation model of water with a dielectric constant of 78.3553, except when comparing to crystal structures, in which case, the gas-phase structure was used. Concentration effects were taken into account as described in the SI (Section S3). The literature value for the solvation energy of a proton is the sum of -264.0 kcal/mol and the -1.9 kcal/mol concentration correction from 1 atm to 1 M.\(^{55,56}\) Potentials for oxidation were calculated and
referred to the calculation for the novel compound 9 in the Cu$^{II}$ and Cu$^{III}$ oxidation states, using the experimental value vs. NHE (1.07 V vs. NHE)$^7$ as recommended in our previous work.$^{57}$ The absolute potential approach of using 4.281 V,$^{14,58-60}$ yields similar results as shown in Section S8 of the SI, though it performs worse for the reference compound 9 which has no isomeric ambiguities, so we do not use it. The potentials of PCET steps are corrected for a pH of 13 using the Nernst Equation.

RESULTS AND DISCUSSION

1. Validation of Model Chemistry

Table 1 shows that the minimum energy structure obtained at the DFT oB97X-D/(def2-SVP,6-31+G(d,p)) level in the gas-phase reproduces the crystal structure of 1. Figure 1 shows that, with this level of theory, either isomer or a combination of both is consistent the UV-Vis absorption features in water.
Table 1. Average theoretical (Theor.) bond lengths, bond angles, and dihedrals of 1 (without hydrogen-bonding waters) in the gas phase as compared to experimental values (Expt).\textsuperscript{7} \textit{intra} indicates a bond angle defined within 1 pyalk ligand whereas \textit{inter} indicates a bond angle defined spanning 2 pyalk ligands.

<table>
<thead>
<tr>
<th></th>
<th>Cu-N</th>
<th>Cu-O</th>
<th>N-O-Cu (intra)</th>
<th>N-O-Cu (inter)</th>
<th>N-C-C-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theor.</td>
<td>1.99 Å</td>
<td>1.89 Å</td>
<td>83.7°</td>
<td>96.3°</td>
<td>0°</td>
</tr>
<tr>
<td>Expt.</td>
<td>1.972(2) Å</td>
<td>1.883(1) Å</td>
<td>84.04(5)°</td>
<td>95.96°</td>
<td>-6.528°</td>
</tr>
</tbody>
</table>

Figure 1. Computed UV-Vis spectra for \textit{trans} (1) and \textit{cis} (2) as compared to the experimental spectrum of a 2 mM sample in water.\textsuperscript{7}
2. Exclusion of Other Mechanisms

In our previous work, we studied the dependence of the peak catalytic current over a wide range of catalyst concentrations and observed no deviations from linearity, even at low catalyst concentrations. This first-order behavior is consistent with a mononuclear mechanism.\textsuperscript{7} We, therefore, did not investigate dinuclear mechanisms such as redox isomerization\textsuperscript{12} or $\mu$-oxo coupling,\textsuperscript{15} which have been proposed for preorganized dimeric catalysts. A reaction between two oxyl radicals is also unlikely, as these species are presumably short-lived and would be expected to undergo mononuclear rather than dinuclear reactions. There is experimental and theoretical evidence to support mononuclear Cu sites in Lytic Polysaccharide Monooxygenase\textsuperscript{61} and Methane Monooxygenase.\textsuperscript{62} Additionally, the stability of the ligand under these oxidizing conditions has been confirmed experimentally in our previous work using CV.\textsuperscript{7} The proposed redox-inactivity of the pyalk ligand is consistent with the deep lying ligand HOMO found theoretically (Figure S9). Thus, we could rule out mechanisms involving a redox-active ligand, such as single electron transfer/water-nucleophilic attack.\textsuperscript{16,17} Therefore, we investigated water-nucleophilic attack as the most plausible mechanism and test it against both theory and experiment; the good agreement that we found validates our approach.

3. The Water-Nucleophilic Attack Mechanism

Scheme 1 shows the mechanism appropriate for basic solutions predicted by DFT calculations, which includes bulk solvation from the dielectric continuum model as well as direct solvation by two hydrogen-bonded waters to the pyalk oxygen atoms.
Scheme 1. Mechanism of water oxidation catalyzed by the complex Cu$^{II}$\(\text{(pyalk)}_2\) (1). The number in superscript indicates the multiplicity.

Step I (Scheme 1) involves the conversion of trans Cu$^{II}$\(\text{(pyalk)}_2\) (1) into the cis form (2), which involves a $\Delta G$ of about 2.8 kcal/mol. So, while there is more trans Cu(pyalk)$_2$ in solution, there is still a catalytically relevant amount of cis form available. The conformational changes induced by the 1→2 conversion are shown in Figure 2.
Figure 2. DFT optimized structures of 1 and 2. The color code is indicated at the bottom of the figure. Hydrogen bonds are indicated by dashed lines.

Step II (Scheme 1) involves oxidation of Cu$^{II}$ to Cu$^{III}$ in the cis form, which includes a first-coordination sphere bond shortening of ~0.11 Å. The experimental potential for this quasireversible conversion is shown to be 1.3 V vs. NHE.\(^7\) The calculated reversible potentials for oxidation of the cis and trans forms are 1.0 V and 1.2 V vs. NHE, respectively. The calculated values for both isomers differ systematically from experiment, likely due to the lack of reversibility in the experimental measurement and the difficulty of modeling the aqueous environment. Intermediate 3 is illustrated in Figure 3.
Figure 3. DFT optimized structures of intermediates 3 and 4 as well as the ion pair and transition states.

Step III (Scheme 1) involves binding of hydroxide to form a cationic five-coordinate Cu$^{III}$ species, 4 (Figure 3), since water deprotonates when attached to Cu$^{III}$. The free energy was computed in two parts, including formation of the ion pair and the actual nucleophilic attack via 3-TS, as shown in Figure 3. The free energy change necessary to form the ion pair is $\Delta G = 5.0$ kcal/mol, dominated by the entropic term ($\Delta S = -23.9$ cal mol$^{-1}$K$^{-1}$), though this energy may be overestimated as ion pairs often form spontaneously in solution. From the ion pair, the free energy change for attachment to Cu is $\Delta G = -15.8$ kcal/mol, leading to an overall free energy change $\Delta G = -10.8$ kcal/mol. The barrier for the nucleophilic attack is 1.0 kcal/mol. Therefore, the barrier for the overall step is $\Delta G^\ddagger_{\text{total}} = \Delta G_{\text{ion pair}} + \Delta G^\ddagger = 5.0 + 1.0$ kcal/mol = 6.0 kcal/mol.

Step IV of the cycle involves formation of the oxyl radical, 5, likely through proton-coupled electron transfer (PCET) at the expense of 1.3 V vs. NHE. The oxidation affects the hydroxyl ligand to form an oxyl radical, rather than forming a high-energy Cu$^{IV}$ species, for which we could not even identify a stable structure as expected from the “oxo wall” principle.
The oxyl-radical intermediate has the structure given in Figure 4 and a spin density of 0.998 on the oxyl oxygen atom while copper has essentially zero spin density (Table S2). The presence of this second oxidation step cannot be ruled out experimentally as estimating the area under the CV trace is complicated by the fact that the reagent (OH\(^-\)) is part of the solvent. Stepwise proton transfer (PT) followed by electron transfer (ET) and the reverse were ruled by evaluating each step separately and finding that the pK\(_a\) of the initial deprotonation step or the potential of the initial oxidation step would be inaccessible under our conditions, as shown in Section S6 of the SI.

![DFT optimized structures of intermediate 5-8 as well as transition state 5-TS.](image)

**Figure 4.** DFT optimized structures of intermediate 5-8 as well as transition state 5-TS.

Step V (Scheme 1) is the nucleophilic attack water on the oxyl radical with a synchronous proton transfer to the nearby alkoxide oxygen of the pyalk ligand (Figure 4). The transition state for that process, 5-TS, and the resulting peroxy intermediate 6 are illustrated in Figure 4, while the mechanism is illustrated in Scheme 2. The net free energy change is \(\Delta G = -20.4\) kcal/mol, and the activation free energy \(\Delta G^\ddagger\) is 19.3 kcal/mol. To compare to the experimental TOF = 0.7 s\(^{-1}\), we used the Eyring equation of transition state theory:
which predicts a barrier of 17.6 kcal/mol. Here, the alkoxide O of the pyalk acts to weaken the Cu-O bond via the trans effect, consistent with the finding that the cis isomer 2 is the active species, as the other pyalk O must be cis to both other O (it is not stable as an axial ligand). Despite our best efforts, we could not locate the equivalent transition state of 5-TS with the N trans to the oxyl radical, though the mechanism should, in principle, be much the same. Instead, we found that this configuration led to an unproductive pathway where the pyalk O attacked the radical instead and the barrier for WNA would be too high (Section S10).

**Scheme 2.** Water-nucleophilic attack (WNA) mechanism onto the oxyl radical of (5) to form (6) upon proton transfer to the pyalk ligand (as shown in Scheme 1).

Step VI (Scheme 1) involves another PCET oxidation on the terminal hydroxyl group, forming a triplet diradical with one spin shared by the two oxygens of the peroxy group (7 as shown in Figure 4), aligned parallel to the spin of CuII. The potential for this PCET is only -0.5 V vs. NHE, making it easily accessible.
Step VII involves triplet oxygen evolution through the mechanism illustrated in Scheme 3, with a modest $\Delta G = 4.0$ kcal/mol, forming a tetrahedral Cu$^{I}$ with one of the pyalk groups still protonated.

Step VIII completes the cycle with another PCET that regenerates the Cu$^{II}$ complex in the cis form, 2. The subsequent oxidation is quite facile, with a potential of -1.1 V vs. NHE. Figure 5 shows the potential surface for the entire mechanism under the conditions of zero bias potential and an operating potential of 1.3 V vs. NHE.

**Scheme 3.** Mechanism of O$_2$ evolution to form (8) according to the reaction mechanism of Scheme 1. Spin alignment is indicated for the terminal oxyl and Cu center.
Figure 5. Free potential energy surface for the water-oxidation reaction catalyzed by (2) under 0 bias (black, $U = 0$ V vs. NHE) and operating condition defined as $U = 1.3$ V vs. NHE (red).

An equivalent mechanism was found with the B3LYP functional (shown in Figures S5 and S6) with the transition state 5-TS becoming just a proton transfer from the water to pyalk. Then two additional structures, A, a minimum, and A-TS, a transition state, for the O–O bond formation (highest point on the surface) were found. The mechanism still involves a water-nucleophilic attack though a predicted barrier of 16.2 kcal/mol (TOF = 8.03 s$^{-1}$).

4. Experimental Corroboration

The mechanism described in Scheme 1 implies that a pyridine-Cu bond is lengthened and ultimately dissociates from the Cu center in intermediates 4–7, opening up a binding site for substrate water. Therefore, a complex with a similar ligand scaffold but without pyridine flexibility should, in principle, be unable to perform catalysis. To test this hypothesis, complex 9
(Figure 6) was synthesized. Like Cu(pyalk)$_2$, complex 9 has two alkoxo- and two pyridyl-groups, but the rigid, tetradentate ligand scaffold does not allow for flexibility of either pyridine and would have difficulty supporting the tetrahedral Cu$^{1+}$ intermediate 8. Under the electrocatalytic conditions used for water oxidation by Cu(pyalk)$_2$, 9 was found not to be competent for water-oxidation catalysis, as shown in Figure 7, thus supporting the catalytic mechanism of Scheme 1.

**Figure 6.** (a) Structure of complex 9 Cu$^{II}$(bipydipyalk)$_2$ and (b) X-ray crystallographic model. Only the asymmetric unit is labeled. Symmetry equivalent atom positions are generated by the operator $\frac{1}{2}$-x, $\frac{1}{2}$-y, z. Thermal ellipsoids are shown at the 50% probability level (SI, Section S1).

Foot-of-the-wave analysis of the catalytic current was used to provide mechanistic information on the chemical step following electron transfer. For a water-nucleophilic attack mechanism in a homogeneous electrocatalytic system, the foot-of-the-wave region can be modeled as follows:

$$i = \frac{4 \times 2.24 \times \sqrt{RT}}{i_p \times 1 + e^{\frac{E_0 - E}{RT}} \times k_1}$$

where, $i$ is the current of the catalytic process, $i_p$ is the peak current intensity of a one-electron non-catalytic process, $v$ is the scan rate, $E$ is applied potential, $E_0$ is the standard potential of the
first electron transfer step, $R$ is the gas constant, $T$ is temperature, $F$ is Faraday’s constant, and $k_1$ is the pseudo-first order rate constant associated with the chemical step following the first electron transfer.

For 1, the linear fit of the foot-of-the-wave region leads to a rate of about $3 \times 10^7$ s$^{-1}$ (Figure 8, Figure S4) while the barrier for the hydroxide nucleophilic attack was estimated to be $5.9$ kcal/mol ($2.8 \times 10^8$ s$^{-1}$) with the $\omega$B97X-D functional and $9.6$ kcal/mol ($5.6 \times 10^5$ s$^{-1}$) with B3LYP, so the experimental estimation is within the range of values predicted by DFT when combined with transition state theory.

![Figure 7](image)

**Figure 7.** CV of 9 in the absence and presence of KOH. Under basic conditions, no enhancement of current above background levels is observed.
Figure 8. Linear sweep voltammogram of 2 mM 1 in 0.1 M KNO₃ adjusted to pH 13 with 0.1 M KOH (black). The region used for foot-of-the-wave calculations is shown in red.

The H/D kinetic isotope effect (KIE) was measured by comparing the cyclic voltammograms of 1 in 0.01 M NaOH and 0.01 M NaOD solution (Figure 9), respectively, both solutions with 0.1 M KNO₃ as electrolyte. The H/D KIE was obtained, as follows:

\[
\text{KIE} = \frac{k_{H,O}}{k_{D,O}} = \left( \frac{i_{H,O}}{i_{D,O}} \right)^2 = \left( \frac{nFA[C]\sqrt{Dk_{H,O}}}{nFA[C]\sqrt{Dk_{D,O}}} \right)^2
\]

where \( i \) = current, \( n \) = number of electrons in the catalytic process, \( F \) = Faraday's constant, \( A \) = surface area of the electrode, \([C]\) = catalyst concentration, \( D \) = diffusion coefficient of the catalyst, and \( k \) = pseudo-first order rate constant. The resulting experimental H/D KIE was found to be 3.4 consistent with proton involvement in the rate-determining step as in the proposed mechanism. The estimated KIE is similar to those found for several other mononuclear copper water-oxidation catalysts but is in stark contrast with those of reported for dinuclear catalysts as shown in Table 2.
Table 2. Literature values for H/D kinetic isotope effects (KIE) for molecular copper water-oxidation catalysts.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nucularity of Cu</th>
<th>KIE</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mono</td>
<td>2.0</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Mono</td>
<td>2.1</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>Mono</td>
<td>1.81</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Mono</td>
<td>2.0</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>Di</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Mono</td>
<td>1.01</td>
<td>69</td>
</tr>
</tbody>
</table>

For comparison, we computed the KIE with exchangeable polar hydrogen atoms swapped with deuterium atoms. We focused on the rate-determining step 5 → 5-TS since chemical steps do not immediately precede it. The resulting KIE was evaluated as in our previous studies, using transition state theory, as shown in Eq. (2).

\[
KIE = \frac{k_{H,O}}{k_{D,O}} = \left( \frac{e^{-(G_{5,H,O} + G_{TS,H,O})/RT}}{e^{-(G_{5,D,O} + G_{TS,D,O})/RT}} \right) = e^{-((G_{5,D,O}) + G_{TS,H,O}) - (G_{5,H,O}) - G_{TS,D,O})/RT}
\]

(2)
The calculated KIE was 3.7, which is in excellent agreement with the experimental value (3.4), further supporting the proposed water-nucleophilic attack mechanism. For comparison, hydroxide binding to Cu$^{\text{III}}$ only exhibits a KIE of 1.1, confirming that hydroxide binding is not rate-limiting.

![Figure 9](image_url)

**Figure 9.** Cyclic voltammograms of 0.5 mM 1 with [NaOH] = [NaOD]=0.01 M. CV’s were taken with boron-doped diamond working electrode, Pt wire counter-electrode, and Hg/HgO reference electrode at a scan rate of 100 mV/s.

Further work to corroborate the proposed mechanism could involve immobilization of catalysts on electrode surfaces and measurements of other catalytic and electrochemical parameters, including $^{16}$O/$^{18}$O kinetic isotope effects under electrocatalytic conditions.
CONCLUSIONS

We have shown that the Cu$^{II}$ (pyalk)$_2$ complex catalyzes water oxidation through a water-nucleophilic attack onto an oxyl radical, formed upon substrate water binding and oxidation by PCET. Remarkably, the pyalk ligand has the ability to remain bound even with a labile pyridine group that opens a coordination site for substrate water binding, enabling robust functionality of a labile first-row transition metal catalyst. The proposed mechanism is supported by measurements of KIE and foot-of-the-wave electrochemical analysis. The resulting insights are particularly valuable for ligand design and development of even more efficient water-oxidation catalysts based on earth-abundant transition metal complexes.

ASSOCIATED CONTENT

Supporting Information. Experimental methods, spin contamination check including spin densities, concentration corrections, additional references and coordinates of structurally optimized molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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