What Determines Catalyst Functionality in Molecular Water Oxidation? Dependence on Ligands and Metal Nuclearity in Cobalt Clusters

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ABSTRACT: The metal-oxo M₄O₄ "cubane" topology is of special significance to the field of water oxidation as it represents the merging of bioinspired structural principles derived from natural photosynthesis with successful artificial catalysts known to date. Herein, we directly compare the rates of water oxidation/O₂ evolution catalyzed by six cobalt–oxo clusters including the Co₄O₄ cubanes, Co₃O₄(OAc)₃(bpy)₃ and [Co₄O₄(OAc)₃(bpy)]⁺, using the common Ru(bpy)₃²⁺/S₂O₈²⁻ photo-oxidant assay. At pH 8, the first-order rate constants for these cubanes differ by 2-fold, 0.030 and 0.015 s⁻¹, respectively, reflecting the number of labile carboxylate sites that allow substrate water binding in a pre-equilibrium step before O₂ release. Kinetic results reveal a deprotonation step occurs on this pathway and that two electrons are removed before O₂ evolution occurs. The Co₄O₄ cubane core is shown to be the smallest catalytic unit for the intramolecular water oxidation pathway, as neither "incomplete cubane" trimers [Co₃O(OH)(OAc)₃(bpy)]⁺ and [Co₃O(OH)₂(OAc)₂(bpy)]⁺, nor "half cubane" dimers [Co₂(OH)₂(OAc)₂(bpy)]⁺ and [Co₂(OH)₃(OAc)₃(bpy)]⁺ were found capable of evolving O₂, despite having the same ligand sets as their cubane counterparts. Electrochemical studies reveal that oxidation of both cubanes to formally Co⁴(III,IV) (0.7 V vs Ag/AgCl) occurs readily, while neither dimers nor trimers are oxidized below 1.5 V, pointing to appreciably greater charge delocalization in the [Co₄O₄]⁵⁺ core. The origin of catalytic activity by Co₄O₄ cubanes illustrates three key features for water oxidation: (1) one four-electron redox metals, (2) efficient charge delocalization of the first oxidation step across the Co₄O₄ cluster, allowing for stabilization of higher oxidizing equivalents, and (3) terminal coordination site for substrate aquo/oxo formation.

INTRODUCTION

Water oxidation catalysts based on first row transition ions are widely sought as replacements for costly noble metal catalysts. Numerous examples of molecular catalysts have been studied which operate over a wide range of cluster nuclearities, ligand functionalities, kinetic activities, and energy efficiencies. Systematic studies within families of related catalysts have uncovered mechanistic complexities that have hampered understanding the factors that influence the rate of O₂ production and the catalyst lifetime.

As a reference point, oxygenic photosynthesis is capable of photo-oxidizing water far faster than any artificial catalyst based on first row transition metals. A recent analysis of the 1.9 Å resolved crystal structure of Photosystem II has shown that nature’s universally conserved water oxidation catalyst is a CaMn₂O₅ cluster best described as a CaMnO₄ “heterocubane” with an O–Mn “dangler.” As result, molecular tetrametallic clusters are increasingly reported as water oxidation catalysts. Among these, the Co₄O₄ cubane structure has been found highly active among metal–oxide molecular catalysts. It also serves as a simplified model for several heterogeneous metal oxide catalysts that contain cubical Co₄O₄ and Mn₄O₄ subunits, respectively, notably the spinels Co₃O₄ and Co₃MnO₄, cubic LiCoO₂, and studies which conjecture that cubic structures may form in the amorphous Co–Pi catalyst.

A particularly clear example of the benefit of the cubical topology for catalysis is seen among the two polymorphs of LiCoO₂ which differ by 100-fold in catalytic activity. Layered LiCoO₂ is made up of alternating layers of cobalt oxide composed of “incomplete cubane” Co₃O₄ replicas, and lithium oxide layers. This material is catalytically inactive. By contrast, active cubic LiCoO₂ is composed of Co₄O₄ cubes stitched together by lithium ions at the corner oxos. This research inspired us to analyze clusters resembling fractions of the Co₄O₄ cubane to determine the required Co nuclearity and other properties needed for catalysis.

In this work we examine the influence of cluster nuclearity and ligand type on the kinetics of water oxidation among the six...
cobalt clusters depicted in Scheme 1. These compounds represent the gradual building of the M₄O₄ cubical core of interest within the same ligand sets (acetate and either pyridine or bipyridine). These clusters include two cubanes, Co₄O₄(OAc)₄(py)₄ (1A) and [Co₄O₄(bpy)₄(OAc)₂]²⁺ (1B), two "half-cubane" dimers, [Co₂(OH)₂(OAc)₃(py)₄]⁺ (2A) and [Co₂(OH)₂(OAc)₃(bpy)₂]⁺ (2B), and two "incomplete cubane" trimers, [Co₃O(OH)₂(OAc)₃(py)₅]²⁺ (3A) and [Co₃O(OH)₃(OAc)₂(bpy)₃]²⁺ (3B). Table 1 lists the Co–Co, Co–O, and estimated O–O bond distances for each of these materials based on previous single crystal X-ray diffraction studies.²³–²⁵ All bond lengths are remarkably conserved throughout these clusters, indicating no major structural changes apart from nuclearity per cluster. We report that there is a clear correlation between cluster nuclearity, ligand lability, and catalytic activity among these materials. Specifically, both cubanes 1A and 1B are active catalysts for oxygen evolution, differing in specific rates according to the number of labile carboxylate ligands. By contrast, the lower nuclearity clusters are inactive catalysts. Trimer 3A and dimer 2A possessing pyridine ligands undergo ligand dissociation that triggers rearrangement to cobalt–oxo oligomers that are active catalysts. These results have significant implications toward understanding the molecular basis by which other reported cobalt complexes may oxidize water.

### RESULTS

**Catalytic O₂ Evolution from Cubes 1A and 1B.** There are several reports of homogeneous water oxidation by 1A, using the widely adopted photoassay depicted in Scheme 1.¹³⁻¹⁵ In light of these reports, 1B became an interesting candidate to study because the Co₄O₄⁴⁺ core structure is conserved, but the nature of the coordinating ligands is different. The clusters also differ in charge: 1A is neutral as isolated, while 1B is dicationic. To our knowledge, 1B has not been studied for water oxidation catalysis.

We prepared 1B as a perchlorate salt according to the literature method.²³ Composition, structure, and purity were established by ¹H NMR, ESI-MS, cyclic voltammetry (CV), and UV–vis (Supporting Information Figures S1–S4). Figure 1 shows the resulting O₂ evolution traces when 1A and 1B are used as catalysts with the photoassay of Scheme 1 (pH 8, 0.05 M borate buffer, 1 mM Ru²⁺, 5 mM persulfate), and dissolved O₂ was monitored by a Clark-type electrode. The amount of O₂ detected exceeded the oxygen content of 1B at all concentrations measured, indicating that its generation is

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**Scheme 1. Compounds and Photoassay Used in This Article**

![Scheme 1 Compounds and Photoassay](image)

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**Table 1. Selected Atomic Distances from X-ray Diffraction.²³–²⁵**

<table>
<thead>
<tr>
<th>cluster</th>
<th>O–O distance⁶</th>
<th>range of Co–O distances, Å</th>
<th>range of Co–Co distances, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>2.56</td>
<td>1.860–1.872</td>
<td>2.696–2.824</td>
</tr>
<tr>
<td>1B</td>
<td>n/a</td>
<td>1.863–1.895</td>
<td>2.663–2.850</td>
</tr>
<tr>
<td>2A</td>
<td>2.50</td>
<td>1.885–1.893</td>
<td>2.811</td>
</tr>
<tr>
<td>2B</td>
<td>2.56</td>
<td>1.883–1.901</td>
<td>2.793</td>
</tr>
<tr>
<td>3A</td>
<td>2.49</td>
<td>1.862–1.906</td>
<td>2.780–2.791⁶</td>
</tr>
<tr>
<td>3B</td>
<td>2.65</td>
<td>1.880–1.919</td>
<td>2.717–2.874</td>
</tr>
</tbody>
</table>

Notes:
- "Estimated, this work (see Supporting Information)."⁶
- We exclude Co–Co not bridged by OH⁻.

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**Figure 1.** Top: O₂ evolution profiles for 1A (blue) and 1B (red) in borate. A control with neither catalyst (black) is also depicted. Lower left: The beginning period of illumination. Intercepts of extrapolated lines for 1A (green) and 1B (orange) allow quantification of lag time. Lower right: Profiles of 1A in pH 8 buffers. Conditions: 100 μM catalyst, 1 mM Ru(bpy)₃²⁺, 5 mM S₂O₈²⁻, 0.05 M buffer, pH 8.
catalytic in nature and not due to stoichiometric decomposition. This conclusion is further supported by the absence of O2 production in the control lacking either cubane (Figure 1).

When considering cobalt based homogeneous water oxidation catalysts, experiments are required to ensure that the nascent molecular cluster, not decomposition products or cobalt oxide nanoparticles, is the sole source of catalytic O2 evolution. As 1A has been shown to be stable in the photocatalytic media under illumination, we anticipated that 1B would be stable as well. To prove this, we compared 1H NMR of 1B alone (Figure 2 bottom trace), Ru(bpy)3 2+ and NaOAc (middle trace), and the contents of the photoassay after 10 min of O2 evolution from 0.01 M borate buffer in D2O (top trace). The fact that all peaks present after catalysis can be assigned to either Ru(bpy)3 2+ or 1B, and not free acetate, confirms that 1B is the source of catalytic O2 evolution, rather than a decomposed species. ESI-MS also confirms the presence of 1B in solution after 10 min of catalysis (Supporting Information Figure S5).

When borate buffer is removed from the photocatalysis conditions in Figure 1, neither 1A nor 1B demonstrates catalysis. 1H NMR analysis of this inactive solution revealed that no peaks of intact cubane (1A or 1B) are observed after as little as 5 min of illumination. Thus, photodecomposition of cubanes 1A and 1B is greatly suppressed in borate. This requirement for a chelating buffer like borate (or carbonate) for cubane catalytic activity may be more than only stability against photodecomposition. Mechanistically, this chelate influence could mean that catalysis may proceed via a base-dependent pathway, involving either deprotonation of an intermediate or hydroxide transfer from borate anion, B(OH)2−.

**Comparative Kinetics: Solvent and Buffer.** To test this idea we investigated the dependence of catalytic rate on buffer concentration. Remarkably, addition of borate (pH 8) shows an inverse relation between buffer concentration and O2 evolution rate (Supporting Information Figure S6). While this trend is seemingly counterintuitive, we note that buffer–dye interactions must be present in excess of buffer–catalyst interactions, and that borate is known to accelerate the decomposition of Ru(bpy)3 2+ via first-order kinetics (further, the rate constants for this decomposition compare to our observed O2 evolution constants, suggesting an effect on the same time scale, see below). Further proof of this buffer induced dye decomposition effect is provided in Figure 1, which shows that when borate is replaced at the same pH with phosphate (a faster decomposer of Ru(bpy)3 2+), a dramatic decrease in O2 evolution is observed. Our results agree with a previous report on an observed decrease in quantum yield as borate is replaced with phosphate. Thus, while buffer is required for O2 evolution and cubane stability against photodecomposition, determination of the reaction order dependence on buffer concentration is complicated by the buffer-dye reaction and the self-terminating nature of the photocatalytic process. In light of recent reports regarding the sensitive use of conditions when studying homogeneous cobalt water oxidation catalysts, we paid careful attention to the choice of reaction conditions as described next. For example, the lifetime of the photocatalytic process can be extended to complete consumption of persulfate electron acceptor by using an acetonitrile–water solvent mixture. To directly compare the kinetics of O2 evolution from 1A and 1B we ultimately chose not to pursue this mixed solvent strategy because the potential for one electron oxidation of 1B in acetonitrile (1.09 V vs SHE) is not equal to that of 1A (Supporting Information Figure S4); hence, 1A would receive a thermodynamic advantage. On the other hand, the reduction potentials reported for the 1A′/1A and 1B′/1B couples in water at pH > 4 are identical (1.25 V vs SHE). Thus, while aqueous photoassays do not last to complete persulfate consumption, water-only solvent is used in order to allow for accurate comparison without significant thermodynamic contributions.

Deliberately, we chose not to measure the onset potential for catalytic water oxidation for cubanes 1A and 1B via electrochemical methods, as we are currently unable to unambiguously assign the resulting data to solely the intact clusters. In fact, we have observed catalytic CoO2 films formed on the surface of glassy carbon electrodes as a result of decomposition of the cubanes at high potentials on glassy carbon, and we echo other studies advising caution if considering studying homogeneous cobalt water oxidation catalysis via electrochemical methods.

While we normally use bicarbonate buffer at pH 7 to screen catalysts (see below), this buffer failed to give consistent kinetic results for 1A as previously reported. This is due to poorer solubility windows of the photoassay components in concentrated bicarbonate. Despite the change in ligand environment between 1A and 1B, the CoO2 core remains a catalytically active structure which acts via a base dependent mechanism. Further comparisons between 1A and 1B are presented in the context of the following kinetic analysis.

**Lag Time.** As can be seen in Figure 1, 1B evolves O2 after the lag phase at a slower rate than 1A over the same time scale. For both materials, the concentration curves plateau at ca. 5 min, after which a steady decrease is observed; this is expected given the self-terminating dye system utilized. To begin a kinetic analysis of these plots, we first consider the lag phase for both materials (Figure 1, inset), during which the assay is illuminated but no O2 is evolved. The lag time is determined from the intercept of the linear extrapolated fit with the baseline. Under identical conditions, we did not observe noticeable difference between the lag time of 1A and 1B. The lag times decrease from 15 to 8 s with increasing [Ru(bpy)3 2+] concentration (Supporting Information Figure S7), consistent with a mechanism that attributes the lag to the time required to photogenate the oxidant and transfer holes into the cubane catalyst.

**Rate Constants.** From the slope of the initial linear portion of the plots in Figure 1, the initial rate of O2 evolution (O2/s) is obtained. A plot of these rates (μmol/s) versus concentration of catalyst (μmol) gives a straight line for both cubanes (Figure 3, top), indicating that the observed catalysis is first-order in
both 1A and 1B. Above catalyst concentrations depicted in Figure 3, the O₂ evolution rate was observed to remain unchanged for each cubane. In this region, the [Ru(bpy)]²⁺:[catalyst] ratio is less than 10:1, which we interpret as being nonrepresentative of pseudo-first-order conditions. Hence, because the region in Figure 3 reflects a correlation of rate with concentration of catalyst, the kinetic representation for our data is eq 1:

\[
\text{rate} = k'\text{[catalyst]} \sum_i \text{[oxidant]}_i + C = k'\text{[catalyst]} + C
\]  

(1)

The slope of the lines in Figure 3 is thus the pseudo-first-order rate constant (k') for each cubane. We obtain values of 0.030 for 1A and 0.015 mol for 1B in units of mol O₂ (mol catalyst s⁻¹). However, the y-intercepts are nonzero (C₁A = 0.0011, C₁B = 0.0007 μmol/s) implying the presence of a zeroth-order pathway. As described next, this zeroth-order contribution is a statistically significant contributor to the overall rate description. First, error analysis of the y-intercepts gives 0.0005 ≤ C₁A ≤ 0.0014 (95% confidence) and −0.0002 ≤ C₁B ≤ 0.0012; these ranges indicate a nonzero y-intercept within experimental error. Second, a log/log plot of the data in Figure 3 gives straight lines with slopes of 0.59 for 1A and 0.58 for 1B. This fractional order also indicates the presence of multiple pathways.

Third, we obtain the turnover frequency per catalyst molecule (TOF), by normalizing the rates to the moles of catalyst in solution (Figure 3, bottom). Accurate fits of the data (solid lines) in the resulting plots are constructed only if a significant effect of the nonzero intercept term is included:

\[
\text{TOF}_{1A} = \text{rate}/[1A] = 0.030 + 0.0011/[1A]
\]  

(2)

\[
\text{TOF}_{1B} = \text{rate}/[1B] = 0.015 + 0.0007/[1B]
\]  

(3)

If the nonzero intercept term is omitted, the fit of solely the pseudo-first-order rate constant (dotted lines, Figure 3, bottom) is poor. We conclude that a zeroth-order pathway exists in this system which is not explained by uncatalyzed O₂ production (Figure 1, control trace). As described next, this pathway is explained by the presence of a multistep mechanism derived from the presence of at least two oxidants from the photoassay medium.

As shown in eqs 2 and 3, an inverse relation between TOF and [catalyst] is seen prominently at low catalyst concentrations. This inverse relationship indicates that catalyst molecules compete with each other for the oxidizing equivalents needed to produce O₂. In light of a previous report which suggested that the sulfate radical contributes to oxidizing 1A, we suspected this oxidant to be necessary for O₂ evolution.

The sulfate radical is formed in situ when excited Ru(bpy)³⁺ is quenched by persulfate (Scheme 1). The SO₄²⁻/SO₄²⁻ reduction potential is 2.4 V versus SHE, significantly stronger than Ru(bpy)³⁺/Ru(bpy)²⁺ (1.26 V vs SHE). As a consequence of the high reduction potential, SO₄²⁻ readily oxidizes Ru(bpy)³⁺, 1A, and the Cl⁻ counterion. Two experiments verify that SO₄²⁻ is necessary for O₂ evolution. First, addition of excess (>500 equiv) Ru(bpy)₃(CIO₄)₃ to solutions of 1A failed to produce any O₂ as monitored by Clark electrode.

Second, a series of photoassays in which 5 mM NaCl or NaClO₄ was added prior to illumination was compared to a control with neither salt. As evidenced in Supporting Information Figure S8, addition of NaClO₄ gave a reproducible trace indistinguishable from the control with no NaClO₄, in contrast, NaCl drastically decreased the rate and yield of O₂ evolution. Chloride oxidation is thermodynamically too high (Cl₂/Cl⁻, 1.36 V) to have an impact on any material in the photoassay other than the sulfate radical. Hence, we conclude that, as part of the reaction mechanism, both 1A and 1B are oxidized by the sulfate radical in at least one of the four oxidation steps.

The kinetic results further imply a mechanistic feature. Within experimental error, the zeroth-order constants C₁A and C₁B are both nonzero; however, we cannot distinguish between the two values using their 95% confidence intervals. In contrast, there exists exactly a 2-fold decrease in the observed pseudo-first-order rate constants for 1B versus 1A.

This data strongly implies that a rate-limiting step occurs at a Co–OAc binding site, because the number of these coordination sites decreases by 50%. This result agrees with numerous literature reports of labile acetate ligands. Carboxylate exchange on 1B has been demonstrated synthetically and has been previously utilized to immobilize 1A on functionalized silica. Insights from EPR studies on both 1A e and 1B e show that, upon single electron oxidation, the hole is delocalized predominantly across the CoO₄ core, residually to the pyridine/bipyridine ligands, and not at all to the acetate, also confirming varying electronic interactions of the ligands on the core. In contrast, our own ¹H NMR data...
indicate no observable exchange of pyridyl group ligands on the time scale of catalyst turnover. To our knowledge, there are no reports of pyridyl group exchange for either cubane.

Because a base is required for catalysis, we thus conclude that binding of substrate water or hydroxide to a carbonylate site (i.e., an oxo-transfer step) is part of the catalytic mechanism. When coupled to the proof that two species oxidize the cubane, it follows that this oxo-transfer step may occur before or after either oxidation step. These observations thus account for the presence of two observed pathways, one major (in which most catalyst molecules proceed via certain intermediates) and one minor (in which a small amount of catalyst molecules proceed via other intermediates).

One observation which may unify these views is that we cannot eliminate hydroxyl radicals (produced from the quenching reaction of the sulfate radical on water or OH−) as the additional oxidant.38 This will be elaborated in the discussion.

No Water Oxidation from Incomplete Cubanes. To test whether binuclear “half cubane” and trinuclear “incomplete cubane” analogues of both 1A and 1B could act as catalysts for water oxidation, we synthesized and tested two dimers, [Co2(OH)2(OAc)3(py)5]PF6 (2A) and a dimer [Co3(OH)2(OAc)3(bpy)3](ClO4)2 (2B), and two trimers, [Co3O(OH)2(OAc)3(py)3](PF6)2 (3A), and [Co3O-O(OH)2(OAc)3(bpy)3](ClO4)2 (3B). Synthesis was conducted by procedures from the literature,23,25 and all clusters were characterized by 1H NMR and ESI-MS (Supporting Information).

Figure 4 compares representative O2 evolution profiles for these clusters as measured by Clark electrode (conditions: 0.1 M bicarbonate buffer at pH 7, 0.5 mM Ru(bpy)32+, 20 mM S2O82− in 90/10 H2O/MeCN. Cluster concentrations 100 μM. Illumination begins at time t = 0.

M bicarbonate buffer at pH 7, 0.5 mM Ru(bpy)32+, 20 mM S2O82− in 90/10 H2O/MeCN compared to a blank photoassay (no cobalt). The results are ligand dependent. Both pyridine species (2A, 3A) exhibit O2 uptake followed by recovery and finally catalytic O2 evolution after a delay. Both other samples (2B, 3B) and the control are not only catalytically inactive, but also indicate the presence of a reaction that consumes O2 below the baseline. Given the almost identical structures of 2A and 2B, we sought to reconcile this data.

Next we present several lines of evidence showing that the pyridyl complexes 2A and 3A actually decompose to a different product which does catalyze water oxidation. In contrast, the more stable coordination of bipyridine to both 2B and 3B prevents photodecomposition, and neither complex is active catalytically.

Decomposition of 2A and 3A. The observation that complexes 2A and 3A take up O2 from solution under illumination during the long lag phase before catalytic O2 evolution, in contrast to the profiles of 1A and 1B, indicates another reaction(s) occurs. For 2A and 3A, the lag times (time to reach the minimum O2 concentration) were in excess of 30 s and often exceeded 1 min, which compares to the lag times for Co3+ → CoOx catalyst under identical conditions.13 The observed lag times thus suggest that decomposition products, not 2A and 3A, are the source of observed O2 evolution.

Further evidence for decomposition of 2A and 3A was obtained by monitoring the photoassay solutions via 1H NMR in 95/5 D2O/CD3CN (Figure S9). Before illumination all peaks can be assigned to intact cluster or Ru(bpy)32+. However, after 10 min of illumination, additional peaks which correlate neither to 2A nor 3A are seen in the pyridine and acetate regions. These new peaks do not correspond to free ligands, thus revealing the presence of new molecular species.

Bulk Electrolysis. Electrochemical oxidation allowed definitive attribution of catalytic activity to decomposition product(s) rather than intact 2A or 3A, in agreement with the results from photoassay studies. Cyclic voltammetry (CV) of 2A and 3A in 0.1 M, pH 7.5 bicarbonate buffer (90/10 H2O/McCN) on glassy carbon shows no significant increase in current relative to a blank CV of pure electrolyte. We then electrolyzed solutions of each compound at 1.05 V versus Ag/AgCl, (similar to the redox potential of the Ru(bpy)32+/3+ couple), and performed cyclic voltammetry of the resulting solutions with a polished separate electrode. This ensures that any changes in the electrochemical response of 2A and 3A were not simply due to the formation of a heterogeneous cobalt oxide film.

The CV traces of 2A taken after 0 (red), 3 (blue), 6 (purple), and 12 (green) min of electrolysis show the gradual appearance of a catalytic wave, illustrating the formation of an active homogeneous or suspended species (Figure 6). A similar change was observed for solutions of 3A (Supporting Information Figure S9). Attempts to isolate and characterize the catalytically active species were unsuccessful. UV–vis of the electrolyzed solutions over time showed disappearance of 2A and 3A absorbance features, but failed to identify any new features. 1H NMR of the resulting solution indicated the presence of multiple molecular species (Supporting Information Figure S10), which were not characterized further. These results indicate that 2A and 3A are inactive as catalysts and photodecompose or oxidatively rearrange into active species.

Catalytically Inactive Bipyridyl Clusters 2B and 3B. By contrast, tests of O2 evolution from the bipyridyl species 2B and 3B (Figure 4) show low level uptake of O2 from the photoassay solution even after 10 min of illumination. This O2 uptake is small (<5%) compared to the yield of catalytic O2 produced by an equivalent amount of either cubane 1A or 2A (Figure 1). We tested this in some detail and found that >50% of the O2 uptake could be attributed to the photoassay medium, as described in Supporting Information (Figures S11 and S12).

The stark differences between 2A and 3A, which decompose to form active materials, versus 2B and 3B which show no O2 evolution, prompted us to investigate the role of the bipyridine ligand in suppressing catalytic O2 evolution. Bpy has been previously noted to poison amorphous CoOx which may form in situ, and can serve as a ligand to determine the origin of.

catalytic activity. Titration of bipyridine into the photoassay medium containing the pyridyl complex 2A (Figure 7) significantly increases the lag time preceding net \( \text{O}_2 \) evolution from 30 s (0 equiv bpy), to 90 s (0.0625 equiv, yellow), to 110 s (0.125 equiv, red). When excess bpy (>5 equiv) is added no net \( \text{O}_2 \) evolution is observed up to 5 min of illumination, and the \( \text{O}_2 \) profiles largely resemble those of 2B and 3B (Supporting Information Figure S13). On the other hand, titration of free bpy into 2B or 3B showed no further changes (Supporting Information Figure S14), indicating that free bpy alone is not responsible for \( \text{O}_2 \) uptake. Thus, we propose that the weak \( \text{O}_2 \) consumption exhibited by 2B/3B, and 2A/3A in the presence of bpy, is consistent with irreversible oxidation of bpy chelated to cobalt, possibly by attack of an oxo/hydroxo ligand on the bpy. Further, bpy chelation to these precursor complexes slows or prevents them from forming the active CoO\(_x\) decomposition product.

**DISCUSSION**

We have shown that, in neutral and near neutral pH conditions, two fully assembled cubane motifs, 1A and 1B, are intrinsically active catalysts for water oxidation, and that their relative rates scale precisely with the number of labile carboxylate sites. By contrast, molecular cobalt–oxo clusters of lower nuclearity (half cubane dimers and incomplete cubane trimers) are catalytically inactive, even though both dimers and trimers have bridging oxos and labile carboxylate sites where terminal water molecules may exchange. Comparing the activity of the compounds tested in this study to the structural parameters listed in Table 1 reveals that the \( \text{O}_x\)-\( \text{Co}-\text{O} \), and \( \text{Co}-\text{Co} \) bond distances are largely conserved across all clusters tested. Thus, no major changes in bond distances are responsible for the sudden appearance of \( \text{O}_2 \) production as Co nuclearity increases to four in both these series. We conclude that a four-electron oxidation pathway is not accessible in these dimers and trimers, and that the Co\(_4\)O\(_4\) cubane topology provides the necessary pathway for activation and \( \text{O}_x\)-\( \text{O} \) bond formation.

Our report of inactivity from organo-cobalt clusters with nuclearity less than 4 stands in contrast to reports of catalytic activity from several organo-Co\(_2\)O\(_2\) dimers \(^{28,43-48}\) and Co monomers. \(^{28,43-47}\) The proposed mechanisms for these materials from their original literature are presented in Scheme 2. To our knowledge, a nucleophilic attack mechanism of water or hydroxide is proposed for all the catalytic monomers. \(^{28,43-47}\) Since these studies are performed at pH \( \geq 7 \), we depict hydroxide as the attacking substrate (Scheme 2, top) for simplicity. The oxidation state of the catalyst that is immediate precursor to \( \text{O}_x\)-\( \text{O} \) bond formation is uncertain, and different claims have been made. For example, Berlinguette et al. and Sartorel et al. postulate Co\(^{4+}\)--OH and Co\(^{5+}\)--OH, respectively, in their systems; \(^{28,43,45}\) these are both formally 1e\(^-\) above a Co\(^{3+}\)--OH moiety. On the other hand, Nocera et al. and Groves et al. propose 2e\(^-\) above Co\(^{4+}\)--OH in their systems; their catalysts are abbreviated \(^{\cdot}\text{L}--\text{Co}^{4+}\)--OH, where the second hole is ligand-centered. \(^{46,47}\) The reasons for these
differences are not known, but may reflect their different coordination environments.

It becomes apparent upon increasing cobalt nuclearity that multiple metals may contribute to the O−O bond formation step, as opposed to tailoring the electronic environment around a single, active metal center. This is evidenced in the proposed mechanism for the known dimer catalysts (Scheme 2, middle). [Co(L)]2(μ-μ-O2O)3+ (L = terpyridine or bis-N-methyl-imidazoyl)pyridine, bpp = bispyridylpyrazolate) each contains a bound peroxy, Co3+−O−O−Co3+, when isolated.42 We label this structure 4 in Scheme 2. During catalytic turnover, the proposed reduced intermediate 4H2 consists of two terminal Co3+−OH groups. The first two oxidations generate two Co3+−O• in which the unpaired electron occupies an antibonding 2π orbital on oxygen. (This electronic configuration is formally equivalent to Co3+μ=O, in which an electron is promoted from a filled 3dσg orbital on Co to fill the π bonding orbital to oxygen that is denoted by the double bond. An unpaired electron exists in the (3d)2t2g5 orbitals on Co, formally denoted Co4+. For simplicity, we retain the oxo radical notation here.) Unlike the nucleophilic attack mechanism, the peroxy bond is formed via coupling of the two Co3+−O• groups. This mechanism has been postulated to occur for the Co3O4 cubane with an energy barrier of 2.3 kcal/mol based on DFT calculations.48 (Scheme 2, bottom). We note that this cross-coupling mechanism indirectly implies that a single Co3+−O• (equivocally Co4+μ=O) is insufficient to oxidize water via a nucleophilic attack mechanism. This is substantiated by several Co3+−OOR alkylperoxide systems, in which the Co3+−O• generated by homolytic bond cleavage is a weaker oxidant of hydrocarbons than the counterpart *OR.49−51

Applying these parameters to our system, we note that all intramolecular O−O bond distances are conservatively estimated to be ca. 2.5 Å, a full angstrom longer than peroxy bonds (Table 1). For this reason, intramolecular coupling between bridging O−O is unfavorable in any of our compounds (active and inactive). An alternate possibility for intramolecular terminal O−O coupling can be envisioned (as in Scheme 2, bottom). However, this requires full dissociation of a (bidentate) acetate, and must occur over Co−Co distances in the range ca. 2.6−2.8 Å (Table 1). A recent study reports only a small contraction (0.03 Å) of some Co−Co distances from 1A to 1A′, indicating this Co−Co distance remains relatively long upon hole injection.52 Combined with the lack of free acetate detection in solution, these lines of evidence suggest that the catalytic mechanism for 1A and 1B is not cross-coupling of two Co3+−O• moieties. From this we conclude that intramolecular O−O bond distance is the primary structural feature needed for water oxidation by cobalt dimers.

We propose that efficient hole delocalization, which facilitates buildup of oxidizing equivalents on cobalt, is the defining property of catalysis from the Co3O4 cubane. This is emphasized for 1A in acetonitrile, where an electron can be removed electrochemically from the core at ca. 0.7 V versus Ag/AgCl, reversibly forming Co3(III,IV). In contrast, electrochemical hole injection into either 2A or 3A is not seen up to 1.5 V versus Ag/AgCl (Supporting Information Figure S15). This effect we believe is more intrinsic to the core type as opposed to the varying cluster charge (1A is neutral, 2A and 3A are cations) because the 2+ cation 1B is also reversibly oxidized within this window (Supporting Information Figure S4).

Our proposed mechanism presented in Scheme 3 accounts for our experimental observations and highlights the effective hole delocalization properties of the cubane structure. The first-order pathway is assigned to oxidation of cubane I by Ru3+; this occurs quickly (107 (M s)−1).14 and hence [1]0 ≈ [11]. Due to the known properties of 11 with both ligand sets, the hole is delocalized across the core, though we depict this in the form of resonance where the hole lies on a cobalt (A) or an oxo bridge (B). Generation of a terminal hydroxide at a carboxylate site then occurs (C), which gives an intermediate that is also
Experimental and computational results suggest that a range of potentials for oxidation of a catalyst containing Co₄⁺–OH is 1.4–1.5 V versus SHE 43,46,48 which is too high for Ru(bpy)₃²⁺ (1.26 V), but not SO₄²⁻ (2.4 V). Thus, the sulfate radical is the only oxidant of sufficient strength to perform the next PCET step on the terminal hydroxide, and a base is required to remove the proton. Depending on resonance, this gives (formally) a terminal Co₄⁺–O₡⁺ (E₁), or one bridging and one terminal O⁺ connected by a Co₃⁺ center (F). The O–O bond formation step thus proceeds via nucleophilic attack of hydroxide in the former case, or oxy–oxy radical coupling in the latter case. We do not yet have single turnover ¹⁸O data that has been proposed by our group to occur in Photosystem II, ⁵³ both mechanisms may occur simultaneously.

As a final note, 1A and 1B compare to the structurally similar Co₄⁺{(hmp)₄(μ-OAc)₂(H₂O)₂} (hmp = 2-hydroxymethyl pyridine) cubane catalyst, but have lower TOFs under similar conditions.⁵⁶ A similar derivative to 1A has been demonstrated to last for 3 times as many turnovers.⁵⁵ We ascribe the slower rates of catalysis from 1A and 1B as due to the need to displace an acetate ligand in order to generate a terminal oxo, as precursor to O₂ evolution. However, the ligand environment of 1A allows for greater catalyst longevity as the terminal aquo/aquo formation is unstable toward decomposition which results in lower turnover numbers.

### CONCLUSION

The molecular clusters studied herein represent discrete models of various cobalt oxide water oxidation catalysts including the solid state spinels. In particular, we have compared the Co₄O₄ cubane structure with smaller subclusters, including Co₅O₉ and Co₆O₁₄ cores, and conclude on the basis of multiple lines of evidence that none of these smaller subclusters is catalytically active for O₂ evolution from water. The origin of catalytic activity by Co₄O₄ cubanes illustrates three key features for water oxidation: (1) four one-electron redox metals, (2) efficient charge delocalization of the first oxidation step across the Co₄O₄ cluster, allowing for stabilization of higher oxidizing equivalents, and (3) terminal coordination site for substrate aquo/oxy formation.

Our findings also illustrate the complexity of the Ru(bpy)₃²⁺/S₂O₅²⁻/photossay, since we have shown that persulfate and buffer are both necessary for catalysis outside of their “standard” roles as sacrificial electron and proton acceptors, respectively.

### ASSOCIATED CONTENT

#### Supporting Information

Detailed synthetic procedures, characterization, illumination profile, and estimation of O–O bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.