Polynuclear Cobalt Complexes as Models of a Cobalt Water Oxidation Catalyst

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(Article begins on next page)
Polynuclear Cobalt Complexes as Models of a Cobalt Water Oxidation Catalyst

A dissertation presented
by
Andrew M. Ullman
to
The Department of Chemistry and Chemical Biology
in partial fulfillment of the requirements
for the degree of
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in the subject of
Chemistry

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Polynuclear Cobalt Complexes as Models of a Cobalt Water Oxidation Catalyst

Abstract

The electrochemical oxidation of Co$^{2+}$ ions in the presence of a buffering species such as phosphate (P$_i$), methyl phosphonate (MeP$_i$), and borate (B$_i$) leads to the formation of amorphous cobalt oxide thin films that are capable of catalyzing the four electron-four proton oxidation of water to dioxygen. These cobalt oxygen evolving catalysts (Co–OECs) have been extensively studied by electrochemical techniques; however, the amorphous nature of these films means that garnering insights at the molecular and atomic level is difficult because electronic and structural characterization methods rely on measurements of bulk material. To address this challenge, polynuclear cobalt hydroxide and cobalt oxide compounds have been employed as platforms for understanding Co–OECs at the molecular level.

In the first part of the thesis, we present the synthesis of a heptanuclear cobalt cluster in two different oxidation states, Co(II)$_7$ and a mixed valence Co(III)Co(II)$_6$. An anomalously slow self–exchange electron transfer rate as compared to that predicted from semiclassical Marcus theory was measured, supporting a charge transfer process that is accelerated by dissociation of the anion from the oxidized cluster. This mechanism sheds light on the inverse dependence of anions in the deposition mechanism of Co–OECs. Moreover, the results address a long-standing controversy surrounding the Co$^{2+/3+}$ self–exchange electron transfer reaction of the hexaaqua complex.

In the second part of the thesis, we report the synthesis and characterization of a dinuclear cobalt complex, which we use as an edge sites mimic (ESM) of the Co-OEC. A comparative
investigation of the P₁ and B₁ binding of buffers to this ESM is provided. We find that the binding to the boric acid component of borate buffer is rapid, while binding to K₂HPO₄ is much slower, taking days to equilibrate at room temperature. These studies are used to provide a model for the interaction of P₁ and B₁ species with the active site of the Co-OEC. An inverse dependence on [B₁] of the electrochemical driven water oxidation activity by Co-OECs is demonstrated, which provides validation for the model and indicates that dinuclear cobalt edge sites are necessary for water oxidation catalysis.

In the final chapter of the thesis, we use a series of spectroscopic and electrochemical methods to show that the observed water oxidation activity of the compound class Co₄O₄(OAc)₄(py–X)₄ emanates from a Co(II) impurity. This impurity is oxidized to produce Co-OEC, which is an active water oxidation catalyst. Differential electrochemical mass spectrometry (DEMS) is used to characterize the fate of glassy carbon at water oxidizing potentials, and demonstrate that such electrode materials should be used with caution for the study of water oxidation catalysis. We then investigate the electrochemical properties of Co₄O₄ cubanes in non-aqueous solvents, showing that the neutral cubanes may be oxidized by two electrons yielding a formal oxidation state of Co(IV)₂Co(III)₂. Finally, we show that these cubanes may be synthetically modified with tethered NMI photooxidants, which opens new avenues for exploring fixed-distance photoinduced ET using Co₄O₄ cubanes as the electron donor. Ultra-fast transient absorption experiments demonstrate that a charge separated state is formed following laser excitation.
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rpm of 2500 (square), 1600 (circle), 1225 (up triangle), 900 (down triangle), and 625 (diamond).

**Figure 3.13** Dependence of $[B_i]$ on the water oxidation current density of 24 mC/cm$^2$ thick films of CoB$_i$ at pH = 9.2 and I = 1 M using a rotating disc electrode at potentials vs. Ag/AgCl of 0.95 V (red), 0.925 V (green), 0.90 V (blue), and 0.875 V (magenta). The shaped data points correspond to rotation rates in rpm of 2500 (square), 1600 (circle), 1225 (up triangle), 900 (down triangle), and 625 (diamond). The slopes of the lines are: $-0.52$ (red), $-0.48 \pm 0.3$ (green), $-0.44 \pm 0.3$ (blue), and $-0.45 \pm 0.1$ (magenta).

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**Figure 4.17** High resolution XPS spectra of the Co 2p\(_{1/2}\) and 2p\(_{3/2}\) region of GC electrodes after a 300 s bulk electrolysis of (red line, —) crude 4.1 (Batch A) at 1.2 V, (blue line, —) purified 4.1 at 1.2 V, and (grey line, —) no analyte at 1.2 V.

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Chapter 1 — Distributed Energy Resources, Water Electrolysis, and the Cobalt Oxygen Evolving Catalyst

Portions of this chapter have been submitted for publication
1.1 The Rise of Distributed Energy Resources

The way we power the planet is changing, and it is changing fast. Currently, most commercial and residential electricity is supplied by grid utilities, which generate power by burning cheap fossil fuels, mainly coal.\(^1\) This long-standing model for energy generation is nearing a tipping point. Distributed energy generation and storage as a primary source of electricity are beginning to supplant the traditional energy infrastructure as the most cost effective way to power our homes.\(^2\) Centralized power plants are giving way to residential, commercial, and utility-scale forms of renewable generation, and a new energy ecosystem is evolving before our eyes.

There are three principle factors driving this transformation in countries like the United States: 1) the installed price per watt of solar photovoltaic (PV) systems has dropped significantly, by \(~7\%\) per year over the past decade,\(^3\) 2) utility electricity prices continue rise as grid operators are forced to invest in an aging infrastructure just to maintain the status quo,\(^4,5\) and 3) consumers want to exert more control over how they use and source their power.\(^6\) As demonstrated in Figure 1.1 (left axis), the price of installation of PV in California has decreased from \(~$12/W\) in 1999 to \(~$5/W\) in 2013. Since California represents the largest U.S. market for PV installations, the price trends nationwide reflect those of this state. There are a number of market forces that have led to such a precipitous decline in price,\(^7\) the most significant being the decrease in module price that has resulted from an increased supply from Asia.\(^8\) However, in recent years, decreases in non-module costs have allowed prices to continue to fall despite small increases in PV module costs.\(^3\) For example, costs related to installation of small scale (\(\leq 10\) kW) roof mounted PVs have significantly fallen as installers have developed new tools to increase the speed at which residential projects are completed.\(^7\)

As a result, the number of solar PV installations in the United States have rapidly increased, with 4800 MW of capacity added in 2013, representing 26% of all new
capacity added in that year. Figure 1.1 (right axis) shows that since 2008 in California the number of residential scale (≤ 10 kW) systems installed each year has roughly doubled every two years. The trend is the same for medium (10-100 kW) and large (> 100 kW) scale PV projects, as well.\(^3\)

Wind power represents another significant renewable energy resource.\(^1\) Installation of wind power capacity has also increased dramatically in the last decade; however, steady year-to-year growth as seen for the PV industry is more challenging because wind projects, being larger in scale, are more tied to incentive programs, which fluctuate depending on the political climate. For example, in 2013 only 1087 MW of new capacity was installed in the United States, as compared to ~13,000 MW in 2012. The key factor in this precipitous drop being a late extension of the production tax credit.\(^9\) Still, wind power is playing a significant role in the evolution of a distributed energy infrastructure.

**Figure 1.1** (Left axis) Median installed price per watt of residential ≤ 10kW PV systems in California. (Right axis) Number of ≤ 10kW PV systems installed in California. Data taken from ref.\(^3\)
Currently, the adoption of distributed energy resources has occurred because consumers are able to couple an environmental motivation, to become less reliant on fossil fuels, with an increasingly favorable economic calculus. In fact, soon the effect of environmental motives may become inconsequential. Utility retail electricity prices are predicted to increase at an annual rate of 3% for the foreseeable future \(^4\) while, as detailed above, solar PV prices continue to fall. As we will discuss in the following section, the costs of batteries capable of being coupled to residential and commercial solar PV systems are also rapidly falling.\(^{10}\) Therefore, for the rational consumer looking to purchase electricity at the lowest price possible, what is the most cost effective way to source electricity?

The Rocky Mountain Institute (RMI) has recently analyzed market data to address precisely this question. Using a series of conservative price assumptions, they were able to model the economically optimal system configuration for supplying electricity to residential and commercial customers.\(^2\) Figure 1.2 presents a summary of their results for the five locations chosen for the analysis. These five locations were chosen because they represent the country as a whole with respect to factors that significantly influence the economics of solar-plus-battery installation, such as insolation and average retail electricity price. For example, a stark contrast is seen between Honolulu, HI where retail electricity prices range from $0.36 – 0.42 (/kWh), and San Antonio, TX where the average price is $0.06 – 0.10 (/kWh). As demonstrated in Figure 1.2, regardless of the location, solar-battery systems rapidly become cost competitive with grid electricity. In three of the five locations, HI, NY, and CA, customers may expect to generate > 50% of their electricity with PV-plus-battery systems within 12 years. By 2050, solar PV supplants the grid as the principal supplier of residential electricity, and a large portion of this electricity generated will be stored prior to being used.
The implications of this analysis for consumers and for utilities are profound. Consumers will benefit from greater choice and with properly timed investment, may shield themselves from rising electricity prices. For utilities, the financial implications of load defection at this scale are potentially devastating. For example, in the northeastern U.S. (i.e., PA, NJ, NY, CT, MA, and RI) the volume of customer load defection from the grid could erode ~ 10-20% of annual energy sales. This lost revenue will severely impact the ability of grid operators to upgrade and maintain their ailing infrastructure. It is therefore not hard to imagine that companies who do not prepare for this eventuality, by for example restructuring rate structure, developing new business models, or pushing for regulatory reform, may be forced to raise their prices at a rate faster than the 3% annual increase used in the RMI model. This will create a positive feedback scenario, forcing even more customers towards load defection, which will put even more stress on

**Figure 1.2** Economically optimal electricity generation mix for residential consumers in Honolulu HI, Louisville KY, Los Angeles CA, San Antonio TX, and Westchester NY Forecasted from present time to 2050. Data taken from ref[2]
the grid operators who do not break from the old paradigm of centralized generation and unidirectional distribution.

These implications for grid operators are not lost on financial stakeholders. Major financial institutions, such as Morgan Stanley and CitiGroup, have issued similar warnings,\textsuperscript{11,12} stating that in developed markets like the U.S. and Germany, it becomes hard to justify continued investment in aging power plants as the demand for electricity continues to fall. Therefore, the industry faces major organizational challenges and must change current remuneration structures to take advantage of new opportunities in an evolving energy climate.

It seems that at least some of the utility companies are listening to these warnings. In Germany, the country’s largest energy supplier, E.ON, announced in late 2014 that it plans to spin off the portion of the company centered on conventional fossil fuels to focus on what the company views as the increasingly important renewable energy sector.\textsuperscript{13} They acknowledged that the impetus for this historic restructuring originates with the rise of marketable renewable technology innovations, like inexpensive PVs, and the increased demand for individualized consumer products. In the U.S., similar restructurings are occurring. For example, NRG, one of the largest energy supplier in the U.S. (servicing 11 states and 3 million retail customers) has recently divided into three subsidiaries, including NRG Home, who’s specific goals are to become the supplier of choice for the millions of tech savvy, young American consumers who a looking to purchase comprehensive residential energy products, such as solar PVs, electric vehicle (EV) charging units, and customizable home energy management systems.\textsuperscript{14,15} The following quote from the CEO of NRG Home, Steve McBee, reveals how this company views the rapidly changing energy landscape:

“The consumer energy markets are on the edge of being significantly disrupted, not unlike the disruption that are occurred with transportation, retail, tourism, and publishing, due to the technology that has been put into the hand of consumers. The take away is what [modern technology] has
enabled, which is the upending of the longstanding, traditional, centralized provider-driven models of service, with consumer-driven, distributed, demand-driven models of service, which have empowered the consumer in the marketplace at the individual level, in ways that are really unprecedented.”

The people want their energy from the sun, and they want to control how they use it.

1.2 Energy Storage at Scale

The rise of affordable energy storage solutions is at the center of the transition to a future of personalized energy. The proliferation of intermittent sources of energy (solar and wind) mandates the need storage. Energy must be available when the sun sets or the wind does not blow. Currently, flow and solid-state battery technologies maintain a dominant position in the energy storage marketplace. However, marketable improvements in these technologies are incremental. Large, disruptive advancements in battery technologies are limited by the finite energy density of the materials used at the battery anode and cathode. For example, the maximum theoretical energy density of a solid-state battery that uses Li-cobaltate as the anode is restricted by the one electron that can be removed from the smallest purposeful unit of the material, specifically a Co(III)O$_2$Li unit. Similar argues can be made for all battery materials, including LiFePO$_4$, which was the prototypical example used in the RMI model discussed above. Anyone who has examined the guts of their laptop will recognize this problem: the battery is always the largest component, dwarfing the computer’s processor and hard drive.

Due to this energy density problem, the only way battery prices can be significantly lowered is through economies of scale. The learning rate, or the cost reduction following a cumulative doubling of production, for this industry is found to be between 6 and 9%\textsuperscript{10}. The most noteworthy example of using economies of scale is with Tesla’s Gigafactory.\textsuperscript{18} Described as a product onto its own by CEO Elon Musk,\textsuperscript{19} the Gigafactory stands to revolutionize the manufacturing process by localizing the battery
supply chain into one 5 million square foot building. Therefore, the raw materials, like lithium and cobalt, will no longer need to travel from one country to another as they are processed into the active materials for the anode and cathode.\(^{20}\)

As important question to address, however, is what happens to the economics of battery manufacturing in a future where all energy is supplied from intermittent renewable sources? Elon Musk has presented an optimistic picture of this eventuality, claiming that with 2 billion of Tesla’s recently unveiled PowerPack batteries, all of the world’s power could be sourced in this way\(^{19}\)

“This is actually in the power of humanity to do. We have done things like this before. It is not impossible, it is really something we can get done. And in fact, we are starting to do it with Gigafactory 1. . . . This is not something Tesla will do alone. Many companies will have to build gigafactory class operations of their own. . . . This is something that we must do, we can do, and that we will do.”

As a celebrity CEO, Musk has a unique podium on which to reach a mass audience, and he is capable of inspiring them to think differently about what can be accomplished with renewable energy. This is a valuable and important trait. However, he is also a business man and so he is inclined to use this power to increase demand in his products. A simple back-of-the-envelope calculation reveals that raw material availability must be considered if batteries are to be scaled to this level. Tesla is expected to use, depending on the application, two different battery chemistries, lithium nickel-cobalt-aluminum oxide (NCA) and lithium nickel-manganese-cobalt oxide (NMC).\(^{21,22}\) We do not know precisely the metal stoichiometries Tesla will use in their cells, but based on available literature for these heavily studied 2\(^{nd}\) generation cathode materials,\(^{23}\) we can reasonably assume that the NCA material will exist as LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.025}\)O\(_2\),\(^{24}\) whereas, the NMC material may rely more heavily on cobalt, with the common mixture being LiNi\(_{0.33}\)Mn\(_{0.33}\)Co\(_{0.33}\)O\(_2\).\(^{25}\)

The amount of cobalt is important because, though we often consider cobalt an earth-abundant transition metal, if batteries are scaled up to the extent that Musk
proposes, the supply of cobalt may become a limiting factor. For example, if we assume that to meet the 200 TWh energy demand, Tesla employs a 50:50 split between NCA and NMC Powerpacks, at 100 kWh per pack, then, as represented in Figure 1.3, 660% more cobalt would be needed than what is currently known to exist in worldwide reserves (see section 1.7 for details of the calculation). Such a demand for cobalt will force mineral suppliers to search for less developed cobalt deposits and to use more economically challenging extraction methods, which will surely push prices up. This could have implications for many industries that require cobalt, such as in aircraft turbine manufacturing and various chemical applications. Likewise, the availability of lithium for battery anodes is also a concern when considering scaling batteries to these magnitudes. We believe that cobalt may have an important role in the future of large scale energy storage, but in order to avoid these resource concerns, it is imperative that most cobalt not be used as a primary source of high energy electrons, but rather as a catalyst for chemical fuel synthesis. In this way, a shortage of cobalt can be avoided.

1.3 Water Electrolysis for Chemical Energy Storage

Water splitting is perhaps the most attractive chemical reaction for storing intermittent renewable energy at large scales because the source of fuel, water, is

![Figure 1.3 Comparison between worldwide cobalt reserves and the amount of cobalt needed for 200 TWh of Tesla NMC/NCA Powerpacks.](image)
ubiquitous. Furthermore, by pairing electrons in chemical bonds, namely the O–O bond and H–H bond, more energy can be stored in a smaller mass—the molecules of oxygen and hydrogen—which greatly increases the maximum theoretical energy density as compared to active battery materials. The thermodynamic potential for the water splitting reaction is given in eq. 1, and its constituent half-reactions are given in equations 1a and 1b.

\[ \text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad E_{OER}^0 = 1.23 \, \text{V} - 0.059 \, \text{V} \times \text{pH} \quad (1a) \]

\[ 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2 \quad E_{HER}^0 = 0 \, \text{V} - 0.059 \, \text{V} \times \text{pH} \quad (1b) \]

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2 \quad E^0 = E_{HER}^0 - E_{OER}^0 = -1.23 \, \text{V} \quad (1) \]

This E° voltage defines the minimum amount of energy that is required to carry out the water splitting reaction, and the maximum amount of energy that can be stored and later recovered, in the bonds of H₂ and O₂. However, driving this reaction (eq. 1) towards the products requires an additional voltage in excess of E°, which is termed the overpotential (\( \eta \)). Minimizing this overpotential is crucial for maximizing the efficiency of a solar–fuels device. Of the two half reactions (eqs. 1a and 1b), the four electron, four proton oxidation of water to dioxygen (i.e. the oxygen evolution reaction, OER) is the more kinetically challenging reaction, and therefore driving this reaction at any given rate, typically demands a more substantial input of overpotential than the hydrogen evolution reaction, HER (eq. 1b).

Existing methods used to split water commercially (mainly for the production of high purity H₂) involve the use of proton-exchange membrane (PEM) electrolyzers that operate in acidic electrolytes, alkaline electrolyzers that operate in strongly basic solution, and solid-oxide electrolyzers that operate at high temperatures of ~1000 °C. In all cases, water splitting is carried out under very harsh conditions, and as a result the cost of the overall balance of systems cost is too high to allow these technologies to scale in an economically feasible way.
This is especially true for small scale water electrolysis systems. As shown in Figure 1.4, as commercial electrolysis technologies are shrunk to meet the more personalized needs of customers, the price of producing H\textsubscript{2} dramatically increases.\textsuperscript{31} This results from a substantial increase in the capital costs (73 % of the total cost) of these systems. Within the contributors to the capital costs, the stack is by far the most costly element, followed by power electronic and then gas conditioning.\textsuperscript{32} Therefore, recommendations for decreasing the cost of small scale electrolysis systems have focused on the stack and pursuing simplified designs, better suited for mass production. As with batteries, electrolysis technologies have much to gain from economies of scale.

One approach to making personalized water electrolysis components more amenable to mass production is to develop systems that can operate under benign conditions, such as at intermediate (close to neutral) pH. Furthermore, systems that are
functional in neutral pH regimes may be more readily incorporated with new technological applications that are incompatible with traditional water splitting methods. For example, catalysts can be interfaced directly to light harvesting systems,\textsuperscript{33,34} incorporated into CO\textsubscript{2} reduction schemes (which perform best at pH = 7), or paired with living components to create inorganic|biological hybrid systems.\textsuperscript{35} To this end, we have emphasized the design and development of catalysts capable of minimizing the overpotential required to drive the OER and that are functionally stable under benign conditions.

### 1.4 Thin Film Cobalt-based Water Oxidation Catalysts

With the above consideration in mind, water oxidation catalysts based on cobalt were targeted. Early work in this area led to the important initial finding that catalytically

![Figure 1.5](image)

**Figure 1.5** Cyclic voltammogram using a glassy carbon working electrode, 50 mV/s scan rate, of aqueous 0.5 mM Co\textsuperscript{2+} in 0.1 M Pi electrolyte, pH 7.0 (--, black), 0.1 M MeP\textsubscript{i} electrolyte, pH 8.0 (-- -- --, blue), and 0.1 M Bi electrolyte, pH 9.2 (-----, red). Background traces in each electrolyte medium in the absence of Co\textsuperscript{2+} are overlaid. Inset highlights the anodic pre-feature on an expanded current scale. Figure adapted from ref\textsuperscript{38}.
active cobalt-based thin films could be formed on inert conducting electrodes upon anodic polarization at > 1.0 V (vs. NHE) in pH 7 phosphate (P_i)-buffered solutions containing sub-millimolar concentrations of simple Co^{2+} salts. Following these initial results, cyclic voltammogram (CV) experiments in Co^{2+}-containing solutions at pH 7, 8 and 9.2 (Figure 1.5) demonstrated that films were formed, not only from P_i buffered solutions, but also those containing methylphosphate (MeP_i) and borate (B_i) electrolytes. The presence of the electrolyte was observed to be essential for formation of films at low potentials as well as for their long-term stability. In the CVs, anodic pre-features (Figure 1.5 inset) are observed that are well separated from a subsequent catalytic wave, which is a result of oxygen evolution. The initial anodic pre-feature (Figure 1.5) is associated with the kinetics of catalyst formation; after catalyst deposition, subsequent CVs in Co-containing or Co-free electrolytes display broader waves that are representative of the redox changes within the electrodeposited film. While we collectively term these oxygen evolving catalyst films Co-OEC, they may be further distinguished as CoP_i, CoB_i, and CoMeP_i depending on the electrolyte used during electrodeposition and catalysis.

The structures of these self-assembled Co-OECs were probed by ex-situ and in-situ X-ray absorption spectroscopy methods and attendant atomic pair distribution function (PDF) analysis. In-situ cobalt K-edge extended X-ray absorption fine structure (EXAFS) studies of thin films of CoP_i established an initial model for the Co-OECs consisting of edge-sharing molecular cobaltate clusters (MCCs). Tiede and co-workers employed PDF analysis to shed more light on the coherent domain size and structure of CoP_i. Their results indicate that atom pair correlations persist out to about 13 Å, and PDF patterns were fit to a model consisting of a 13-14 Co atom lattice domain consisting of edge-sharing CoO_6 octahedra, in good correspondence with the in situ EXAFS results. Phosphate was found as a disordered component in the films, and minority “defect” sites consisting of complete Co_4O_4 cubanes were also proposed. In
addition, the PDF data suggested that the clusters might possess distorted coordination geometries at their periphery, such as alterations in the terminal O ion positions. It was proposed that these terminal Co–O distortions could play a key role in O₂ evolution catalysis at CoPᵢ by facilitating the formation of terminal peroxo intermediates.

X-ray PDF analysis was further employed to explore the influence of deposition conditions on the structure of Co-OEC films. These studies established that the nature of the buffering electrolyte (Pᵢ and Bᵢ) affects the intermediate range structure of the catalyst. The refined PDF fits and models for CoBᵢ and CoPᵢ catalysts are shown in Figures 1.6a and 1.6b. Films of the CoBᵢ comprise three layers on average of the MCC, and the diameter of the layers is approximately 35 Å. Constraining the model to a single layer results in a poorer fit suggesting that the coherent domains of CoBᵢ do indeed consist of multiple layers of MCCs with weak, but significant interlayer correlations. The PDF data also revealed a significant interlayer expansion as compared to crystalline CoOOH, possibly to accommodate something larger than protons in the interlayer region such as weakly scattering or disordered electrolyte ions, though Bᵢ was not identified explicitly. The refined CoPᵢ model and fit (Figure 1.6b) indicates that the diameter of the clusters is approximately 14 Å, considerably smaller than those of CoBᵢ. Unlike CoBᵢ, modelling PDF data could not accommodate layers of CoPᵢ, suggesting that the coherent domains of the catalyst consist of single layer MCCs whose arrangements are significantly disordered in the film. In chapter 3, we present a comparative study of the kinetics and thermodynamics of Pᵢ and Bᵢ electrolyte binding to the surface a molecular model of the Co-OEC’s edge-sites. These results are then used to explain the origin of the structural difference observed in Figure 1.6.
X-ray absorption near edge structure (XANES) studies in conjunction with electron paramagnetic resonance (EPR) spectroscopy methods have been particularly useful for developing a coherent picture of the valency of these Co-OEC films—particularly of the resting state, which is the predominant form of the catalyst during turnover. XANES spectra of CoP$_i$ samples collected in situ during catalysis at 1.25 V were compared with the spectra of solid samples of reference compounds CoO and CoOOH. The observed edge positions for the CoP$_i$ samples are consistent with an average Co valency $\geq 3$ at 1.25 V, indicative of some formal Co$^{IV}$ valency in the resting state. McAlpin et al.$^{43}$ and Gerken et al.$^{44}$ conducted EPR studies of CoP$_i$ samples freeze-quenched after deposition at a variety of potentials. Continuous wave (CW) X-band EPR spectra of frozen catalyst samples display a broad resonance at $g_{\text{eff}} \approx 5$ along with a broad
derivative lineshape at $g_{\text{eff}} = 2.27$ (Figure 1.7). The $g_{\text{eff}} \approx 5$ feature was assigned to an $S = 3/2$ Co$^{II}$ species based on EPR spectra of model Co$^{II}$ compounds. The progressive rise of the $g_{\text{eff}} = 2.27$ feature as the deposition potential is increased along with its similarity to the $g$ value of the signal observed in a tetracobalt cubane model compound ([Co$_4$O$_4$(OAc)$_4$(py)$_4$](ClO$_4$)) possessing Co centers with formal oxidation states of III, III, III, IV (Figure 1.7b), provides strong evidence for the assignment of the $g_{\text{eff}} = 2.27$ signal to low-spin Co$^{IV}$-containing species in the catalyst film. Moreover, the potential dependence of this signal suggests that it arises predominantly from species generated during electrocatalytic water oxidation, corroborating the finding of the in situ XANES study. Taken together, the results from the XAS, PDF, and EPR studies are consistent with polynuclear active sites in which some fraction of Co centers achieve a formal
oxidation state of +4 at potentials sufficient for water oxidation catalysis, indicating a Co$^{III/IV}$ mixed valence resting state during oxygen evolution.

Returning to the CVs in Figure 1.5, it can be seen that current due to film formation and to O$_2$ evolution catalysis exhibit different dependencies on pH, with the anodic pre-feature, associated with deposition kinetics, shifting to a greater extent in a cathodic direction as the pH is increased from 7 to 9.2. This separation in potentials was an early indication that the two processes are distinguished by unique electrochemical mechanisms; therefore, steady-state electrokinetic data were acquired over a range of electrolyte conditions, in order to uncover the electrochemical rate laws for both O$_2$ evolution$^{45}$ and catalyst deposition.$^{46}$

Tafel plots, which describe the variation of the steady state current density with the potential or overpotential supplied at the electrode,$^{47}$ provide key mechanistic insights for electrochemical reactions that are not mass-transport limited. Under these conditions, the current density measured at steady state is directly proportional to the rate of the underlying electrochemical reaction. A Tafel slope of nearly 59 mV/decade was observed for the thin CoP$_i$ films, indicating a reversible one-electron minor equilibrium step followed by a turnover-limiting chemical step.$^{47}$ Subsequent examination of the pH dependence of OER rate by both potentiostatic and galvanostatic techniques were

![Diagram](image.png)

**Figure 1.8** Proposed mechanism for OER by CoP$_i$. A PCET minor equilibrium proceeded by a turnover-limiting O–O bond forming step is consistent with current dependencies on proton and electron equivalencies. Adapted from ref.$^{45}$
consistent with an inverse first-order dependence on proton activity, indicating that proton transfer is coupled to the equilibrium ET step.\(^{45}\)

A zeroth order dependence of phosphate was observed over a >1.5 decade range of phosphate concentration indicating that proton transfer to phosphate is not involved in the turnover-limiting step and that phosphate is neither a reactant nor product in the overall water oxidation mechanism (other than as a proton acceptor). These findings are summarized in the electrochemical rate law for OER (eq 2, Table 1.1) and, in conjunction with the known resting state valency provided by the XANES and EPR measurements, allow for the proposal of a mechanistic scheme for OER, as shown in Figure 1.8.

**Table 1.1** Electrochemical Rate Laws for Co-OEC OER and Deposition

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Electrochemical Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Evolution</td>
<td>( v = k_0^{OER}(a_{H^+})^{-1}\exp\left(\frac{F}{RT}\right) ) (2)</td>
</tr>
<tr>
<td>Catalyst Deposition</td>
<td>( v = k_0^{dep}<a href="a_%7BH%5E+%7D">\text{Co}^{2+}</a>^{-3}[\text{MeP}]^{-1}\exp\left(\frac{F}{RT}\right) ) (3)</td>
</tr>
</tbody>
</table>

In a similar manner, activation-controlled current densities for steady state catalyst deposition were determined as a function of the applied potential, \( \text{Co}^{2+} \) concentration, pH, and buffer (MeP\(_i\)) concentration. In each case, Tafel plots relating applied potential to the activation-controlled current density were obtained over a range of electrolyte conditions. Interpolation of these plots permitted determination of the respective reaction orders in \( \text{Co}^{2+} \) concentration, proton activity, and buffer concentration.\(^{46}\) These studies uncovered a first order dependence on \( \text{Co}^{2+} \) concentration, and, as in the OER reaction, a reversible one-electron equilibrium was implied by the 60 mV/decade Tafel slope. It was also observed that the rate of deposition possesses an inverse third-order dependence on proton activity, and at intermediate buffer strengths, an inverse first order dependence in MeP\(_i\).
Below 2 mM MeP$_i$, a plateau was observed implying that, at these concentrations, MeP$_i$ is no longer explicitly represented in the rate law for electrodeposition. Nevertheless, at high concentrations of buffer, it was proposed that an equilibrium dissociation of MeP$_i$ from the surface was a critical prerequisite for incorporation of newly oxidized Co centers. Thus, the Co(OH)$_2^{2+}$ solution precursor is proposed to undergo a one electron-proton minor equilibrium PCET reaction to form a Co(OH)$_2$(OH)$_4^{4+}$ intermediate. Simultaneously, a surface equilibrium involving MePO$_3^{2−}$ dissociation and the removal of one proton takes place. This heterogeneous equilibrium leads to a surface intermediate poised for rate-limiting binding of the solution-based Co(OH)$_2$(OH)$_4^{4+}$ species to effect catalyst growth by one Co center. These findings are summarized in the electrochemical rate law for catalyst deposition in Table 1.1 (eq. 3) and with the mechanistic scheme in Figure 1.9.

### 1.5 Cobalt Complexes as Models of the Co-OEC

Unlike the amorphous solids of Co-OECs, where structure at the most precise atomistic level is undetermined, inorganic molecular complexes may be structurally characterized precisely using x-ray diffraction. Accordingly, a research program was initiated to use polynuclear cobalt molecules, especially those which oxidic ligands (O$^{2−}$,
OH−, and OH2), as models for the Co-OEC. This approach was partly inspired by the work of bioinorganic chemists, who have for decades synthesized metal complexes as models for redox cofactors and active sites of proteins, most notably, the manganese-based OEC found within PSII. The goals of this program, like those of the bioinorganic chemists, were to use the molecular reactivity and spectroscopic handles of multinuclear molecular cobalt complexes to provide direct comparisons to Co-OEC.

Two relevant examples of this approach preceded the work presented in the following chapters of this thesis; they are summarized now. As discussed previously, EPR studies on the molecular cobalt cubane, Co4O4(OAc)4(py)4+ provided evidence that the EPR signal that arises from Co-OEC at anodic potentials is due to a delocalized Co(IV) valency (Figure 1.7). Additional multifrequency EPR studies and electronic structure calculations were performed on this Co4+-containing cubane compound to interrogate further the electronic and geometric structure relationships of MCCs such as those found in CoP1. The magnetic parameters determined by electron nuclear double resonance (ENDOR) and spectroscopic results from electron spin echo envelope modulation (ESEEM) combined with density functional theory (DFT) calculations revealed that the unpaired spin of the cubane is highly delocalized. Each octahedrally coordinated cobalt ion was found to possess a low-spin electron configuration due to the anionic oxo and carboxylato ligands, and a fractional electron hole resides on each metal center in a Co 3d_{xz,yz}-based molecular orbital, essentially giving a [Co^{3.125}O4] cluster. However, closer inspection of the EPR spectra of the molecular model and those of CoP1 revealed features consistent with less delocalization of the unpaired electron spin in the case of CoP1 compared to the model. It was proposed that since the CoIII/IV redox transformations in the bulk of the film and at active sites during turnover are coupled to proton loss from bound OHx ligands, the increase in ligand-field strength accompanying this proton loss could result in substantial localization of unpaired spin density. This localization of the oxidized equivalent is consistent with subsequent reactivity of the CoIV
moieties in CoP₁ compared to the molecular model (Chapter 4). These findings implicate the importance of PCET not only for redox potential leveling, but also for hole/radical localization, leading to efficient oxygen evolution in Co-OEC films.

The cubane Co₄O₄ core has also provided a platform for the study of the PCET properties associated with charge transfer through the films. The molecule Co₄O₄(OAc)₂(bpy)₄²⁺, 1.1, first synthesized by Christou and coworkers, also contains a Co₄O₄ core, but differs in overall charge from Co₄O₄(OAc)₄(py)₄ in its all Co(III) form, due to the replacement of two acetate ligands by neutral bipyridines. 1.1 exhibits a
reversible Co(IV)Co(III)$_3$/Co(III)$_4$ couple with an $E_{1/2} = 1.25 \text{ V vs. NHE}$ at pH $> 4$. Below pH $= 4$, the $E_{1/2}$ value becomes progressively more positive, exhibiting a slope of $–55 \text{ mV/pH unit}$ at pH $< 2$, Figure 24b. The electrochemical response in the low pH region of the Pourbaix diagram is indicative of a one-electron, one-proton transfer of a protonated species, 1.1-H$^+$, with a $pK_a = 3.1$, to a deprotonated, oxidized cubane, 1.2. Since a second plateau region was not observed at high potentials, the $pK_a$ of the protonated form of 1.2 must be pH $< 0$.

As discussed briefly above, charge transport through Co-OEC films is thought to proceed via electron and proton hopping between Co(III)-OH to Co(IV)-O species. Therefore, we sought to isolate the kinetics of this PCET event by interrogating the mechanism by which 1.1-H$^+$ is converted to 1.2.$^{53}$ We were interested in comparing the bidirectional reaction, in which the electron and proton are transferred to separate chemical species, to the unidirectional reaction, in which they are transferred to the same species. By varying the scan rate in cyclic voltammogram experiments, the heterogeneous ET rate constant was extracted by comparing simulated CV traced with the experimental data. Using this method, it was found that the rate constant for the PCET reaction at pH $= 1$ was $k_{\text{PCET}} = 0.17 \text{ cm s}^{-1}$, an order of magnitude smaller than the simple ET rate constant measured at pH $= 4$, $k_{\text{ET}} = 2 \text{ cm s}^{-1}$. The lack of an observable kinetic isotope effect (KIE) at pD $= 1$ indicated that the PCET reaction at the electrode surface is step-wise, proceeding by an equilibrium proton transfer followed by a rate-limiting electron transfer (PTET). This stepwise pathway was also found to predominate in the bidirectional PCET reaction between [Ru(bpy)$_3$]$^{2+}$ and 3 at pH or pD $= 1$. In this homogeneous reaction, 1.2 was reduced to 1.1-H$^+$ by [Ru(bpy)$_3$]$^{2+}$ with a driving force of $\sim 100 \text{ mV}$. Stopped-flow kinetic measurements resulted in near identical second-order rate constants ($\sim 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) in H$_2$O and D$_2$O. As in the heterogeneous bidirectional PCET reaction, the lack of an observable KIE indicated at stepwise PTET mechanism.
The unidirectional PCET self-exchange reaction between 1.1-H⁺ and 1.2 (Figure 1.10c) was also interrogated using NMR line broadening analysis. The rate constant for this reaction at pH = 1, kSE1 = $5.6 \times 10^4$ M⁻¹ s⁻¹ was found to be only a factor of ~5 slower than the simple self-exchange ET reaction at pH = 4, kSE4 = $3.0 \times 10^5$ M⁻¹ s⁻¹. As a comparison, the expected rate constant at pH = 1 for the stepwise self-exchange PTET reaction constant can be calculated using kSE4 and the acid dissociation constant of 1.1-H⁺ according to equation 4.

$$k_{SE1} = k_{SE4} \frac{K_a}{[H^+]} = 3.0 \times 10^5$ M⁻¹ s⁻¹ $\frac{10^{-3.1} M}{10^{-1} M} = 2400$ M⁻¹ s⁻¹ (4)

Since the calculated rate constant is over a factor of 20 smaller than the experimentally determine value, a concerted proton-electron transfer, CPET, mechanism is implicated for this unidirectional PCET event. This supposition was confirmed by the measurement of a significant KIE = 4.3 for the self-exchange reaction at pH = 1, which suggests that proton tunneling is involved in the rate limiting step. Taken together, these results indicate that the unidirectional pathway for electron and proton hopping between Co(III)-OH to Co(IV)-O species provides an activation barrier that is significantly lower in energy than the intermediates of the stepwise reactions. This result set the stage for a detailed study of the hole transport within Co-OEC films, which was described by a charge neutral electron-proton hopping mechanism (akin to the CPET mechanism of 1.1-H⁺/1.2) between MCCs within Co-OEC. Furthermore, and of particular significance to chapter 2, this study highlighted the value of studying self-exchange reactions for interrogating the details of ET mechanisms with relevance to Co-OEC.

1.6 Scope of Thesis

With this precedent in place, new molecular models of the Co-OEC were targeted. The following chapters are divided on the basis of the nuclearity of the Co complexes under investigation. In Chapter 2, self-exchange electron transfer between Co⁷ cobaltate-
like clusters is investigated, leading to a refined model of the Co-OEC deposition mechanism. In Chapter 3, we present the design and synthesis of a molecule edge-site mimic (ESM) for the Co-OEC. The kinetics and thermodynamics of $P_i$ and $B_i$ binding to the ESM are compared, leading to a model for understanding the interaction of these electrolytes with the active sites within the Co-OEC. Finally, in Chapter 4, we show that the observed water oxidation activity of the compound class $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py}–\text{X})_4$ emanates from a Co(II) impurity. We also demonstrate that in non-aqueous solvents these cubanes may be oxidized by two electrons yielding a formal oxidation state of $\text{Co(IV)}_2\text{Co(III)}_2$, and that these complexes are amenable to post-synthetic modification that has opened the door for exploring fixed-distance photoinduced ET using $\text{Co}_4\text{O}_4$ cubanes as the electron donor.
1.7 Calculation for Cobalt Requirements of Li-ion Batteries at 200 TWh Scale

As an example, we will calculate the amount of cobalt (in metric tons) needed for 1 billion powerpacks, which use NCA (LiNi$_{0.8}$Co$_{0.15}$Al$_{0.025}$O$_2$) as the cathode. Equation 5 calculates the charge (in Ah) associated with this number of powerpacks (100 kWh/pack) and assuming an average operational voltage of 3.7 V. Equation 6 calculates the gram of cobalt present per Ah of active electrons assuming 60% cathode utilization (average depth of charge). ACM stands for active cathode material. Equation 7 presents the multiplication of eq. 5 and 6 to give the final result. A similar calculation can be done for NMC cathodes (LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$) with the only difference being the mole of Co per moles of ACM would change to 0.33.

\[
1 \times 10^9 \text{packs} \times \frac{100 \text{ kWh}}{\text{pack}} \times \frac{1000 \text{ W}}{1 \text{ kW}} \times \frac{A}{3.7 \text{ W}} = 2.7 \times 10^{13} \text{Ah}
\]  

(5)

\[
\frac{58.93 \text{ g Co}}{\text{mol Co}} \times \frac{0.15 \text{ mol Co}}{1 \text{ mol ACM}} \times \frac{1 \text{ mol ACM}}{3600 \text{ C}} \times \frac{1 \text{ mol active e}^-}{0.60 \text{ mol active e}^-} \times \frac{\text{g Co}}{96485 \text{ C} \cdot \text{Ah}} = 0.550 \frac{\text{g Co}}{\text{Ah}}
\]  

(6)

\[2.7 \times 10^{13} \text{Ah} \times 0.550 \frac{\text{g Co}}{\text{Ah}} = 1.49 \times 10^{13} \text{ g Co} = 1.49 \times 10^7 \text{ metric tons Co}
\]  

(7)
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Chapter 2 — Self-Exchange Electron Transfer and Anion Dynamics of Co$_7$ Clusters

Portions of this chapter have been published
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2.1 Introduction

Central to the self-assembly process of Co-OECs, which forms the basis of the self-repair mechanism of the Co-OEC,\(^1\) is the oxidation of Co\(^{2+}\) to Co\(^{3+}\). The importance of anion dissociation in this oxidation process is indicated by the inverse anion dependence in the electrokinetic rate law for nucleation of the Co–OEC catalyst.\(^2\) In attempting to understand the electron transfer kinetics of Co\(^{2+}\) for the Co-OEC self-assembly process, one is confronted with a long-standing and unresolved issue arising from an anomalously high self-exchange rate constant (\(k_{SE}\)) of the Co(OH\(_2\))\(_6^{3+/2+}\) couple, \(k_{SE} = 5 \text{ M}^{-1} \text{s}^{-1}\), which is ~six orders magnitude greater than predictions based on Marcus theory.\(^4\),\(^5\) Two proposals have been put forward to account for the anomalous behavior of the Co(OH\(_2\))\(_6^{3+/2+}\) self-exchange reaction: a high-spin excited state mechanism\(^6\) and a water-bridging mechanism.\(^7\) In the former mechanism, the participation of high spin excited state of Co\(^{3+}\) is invoked, which provides an explanation for how large reorganization energy associated with a Co\(^{3+}\)(low spin)/Co\(^{2+}\)(high spin) crossover could be avoided. Alternatively, a water bridge between the two cobalt centers has been postulated to facilitate electron transfer by increasing the electronic coupling between the metal centers owing to the formation of an inner-sphere complex.

In an effort to distinguish between these two disparate mechanisms, temperature-dependent \(^{59}\)Co NMR spectroscopy was undertaken by Navon on samples of Co(OH\(_2\))\(_6^{3+}\) with the objective of observing a paramagnetic shift owing to the presence of a high spin state.\(^8\) The absence of such a paramagnetic shift sets a lower limit of 23 kJ/mol for the separation between the high-spin \(5\text{T}_{2g}\) excited state and the low-spin \(1\text{A}_{1g}\) ground state. Subsequent thermodynamic calculations were in support of this estimation,\(^9\) supporting the notion that the excited state is too high in energy to participate in the self-exchange reaction at room temperature. Despite this evidence against the excited state mechanism, the water-bridge mechanism, in which the electron transfer takes place through an inner-sphere
pathway, remains conjecture, and to date the mechanism for Co(OH$_2$)$_6^{3+/2+}$ self-exchange electron transfer continues to be uncertain.

Herein, we present the synthesis and characterization of a Co$_7$ cluster that displays the same cobaltate cluster core as that observed for Co–OEC. The ability to prepare the Co(II)$_7$ and mixed-valent Co(III)Co(II)$_6$ clusters permit a Co(II)|Co(III) self-exchange rate constant to be isolated and measured. An intriguing aspect of the self-exchange reaction is its similarity to the Co(II)|Co(III) couple in a hexaaqua-like O-atom ligand field, but with a secondary structure that precludes the involvement of an inner–sphere electron transfer pathway. By comparing the measured $k_{SE}$ to that calculated $k_{SE}$ using semi-classical Marcus theory, we provide evidence to support the involvement of a water-bridging mechanism for the Co(OH$_2$)$_6^{3+/2+}$ exchange reaction. Finally, we show that the six order of magnitude discrepancy between the calculated and measured rate constants for the heptanuclear cluster, results from a specific anion interaction with the cluster core. These results provide insight on the role of anions in the self-assembly process of Co–OEC.

2.2 Results

2.2.1 Synthesis and Characterization of 2.1 and 2.2

The choice of 2-iminomethyl-6-methoxy-phenol (HL) for stabilizing a cobaltate cluster core was motivated by the synthetic method of Zhou et al. that delivers the perchlorate salt of 2.1. The reaction proceeded at a maximal yield of 45.9% using nonstoichiometric reagents under microwave reactor conditions, as an alternative to traditional hydrothermal synthetic methods. Given the fast ligand exchange rates for the Co(II) ion, we surmised that by utilizing the precise stoichiometry of 7:6:12 Co:HL:NEt$_3$, we would be able to cleanly synthesize the desired product at ambient temperatures, as summarized in Figure 2.1 (top). Indeed, under these conditions and at room temperature, we found that the triflate salt of 2.1 precipitated from MeCN:H$_2$O solutions when the water
content was raised above 25%. Elementally pure compound was isolated by simple filtration to remove a minor insoluble impurity. The universality of this procedure was confirmed by its successful implementation in the synthesis of 2.3, the analogous zinc cluster Zn7(OH)6(L)6(O Tf)2, which was previously crystallographically characterized as the nitrate salt.37
The identification of optimum reaction conditions was aided by the distinct NMR spectra exhibited by these compounds. Consistent with the S6 symmetry of the complexes, only one set of ligand resonances was observed. The NMR spectra for all compounds are presented in the section 2.5. The spectrum for 2.1 exhibits broadening and paramagnetic shifts of the signals due to the presence of the high spin Co(II) ions. All but the aldiminic and hydroxide proton resonances were observable. For 2.3, a diamagnetic compound, all proton resonances were observed and exhibit the expected shifts and couplings.

The oxidation of 2.1 to 2.2 proceeded cleanly using the oxidant AgOTf in nitromethane, which solubilizes 2.1, 2.2 and AgOTf, and ensures the full oxidizing potency of the Ag⁺ ion. The formal potential for the 2.1/2.2 couple was estimated by cyclic voltammetry (CV). The CVs of 2.1 and 2.2 at room temperature and in the presence of 0.1 M TBAOTf (Figure 2.2) exhibit broad, electrochemically irreversible waves. The oxidation of 2.1 occurs between 0.4 and 0.6 V while the reduction of 2.2 occurs between –

![Figure 2.2 Cyclic voltammograms of 2.1 (—, 1.0 mM) and 2.2 (—, 1.0 mM) in 0.1 M TBAOTf in acetonitrile solution, using a glassy carbon working electrode. Scan rate 0.1 V/s. The cross and arrow indicates the initial potential and direction of scan.](image-url)
1.0 and –1.2 V (E\textsubscript{pa} = 0.487 V and E\textsubscript{pc} = –1.099 V, all potentials vs. Fc\textsuperscript{+/0}). The formal potential cannot be deduced without more detailed electrochemical experiments, but it can be bracketed as < 0 V, which is consistent with the observation that treatment of 2.1 with 1.5 eq of FcOTf results in conversion to 2.2, as observed by NMR.

Complexes 2.1 and 2.2 co-crystallize from a solution mixture and were characterized using X-ray diffraction analysis. The thermal ellipsoid plots are presented in Figure 2.1. A bond contraction of 0.174 Å between the central cobalt atom, Co(1), and the surrounding \(\mu_3\)-OH ligands is observed upon oxidation. The bond contraction is consistent with a localized Co(III) valency at Co(1) in 2.2, as has been observed in a related structure containing the same Co(III)Co(II)\textsubscript{6}(OH)\textsubscript{6} cluster core stabilized six iminophenylmethoxyphenol ligands.\textsuperscript{13} A comparison between 2.1 and 2.2 of the cobalt atoms’ inner sphere bond distances is presented in Table 2.1. The bond lengths associated with the outer

\begin{table}[h]
\centering
\caption{Comparison of Inner Sphere Bond Lengths}
\begin{tabular}{llll}
\hline
Bond & 2.1 \(d_0\) (Å) & 2.2 \(d_0\) (Å) & \(\Delta d_0\) (Å) \\
\hline
Co(1)–O(1) & 2.092(11) & 1.918(1) & –0.174(11) \\
Co(2)–O(1)\textsubscript{N} & 2.149(16) & 2.219(24) & 0.070(29) \\
Co(2)–O(1)\textsubscript{O} & 2.016(3) & 2.0393(6) & 0.024(4) \\
Co(2)–O(2)\textsubscript{A} & 1.995(9) & 1.969(2) & –0.026(9) \\
Co(2)–O(2)\textsubscript{B} & 2.051(11) & 2.014(4) & –0.037(12) \\
Co(2)–O(3) & 2.395(32) & 2.367(18) & –0.028(37) \\
Co(2)–N & 2.077(2) & 2.056(8) & –0.021(8) \\
\hline
\end{tabular}
\end{table}
cobalt atom, Co(2), change only modestly; the average Co(2)–O/N bond lengths are 2.11 ± 0.15 Å for both clusters. The contraction of the hydroxides around the central Co(1) of 2.2 results in a bond lengthening between the hydroxide ligands and the outer cobalt atoms, Co(2). The lengthening is asymmetric with a 0.073 Å increase for the bond trans to the more electron donating imine group and only 0.024 Å for the bond trans to the weakly donating methoxy moiety. The remaining bonds to the Co(2) atoms contract to compensate for the lost electron density from the hydroxides, but these contractions are slight (≤0.037 Å) owing to the rigidity of the six iminomethyl methoxyphenol ligands, L−.

The Co7(OH)6 cores of 2.1 and 2.2 are coordinated by triflate anions via hydrogen bonding interactions. One triflate anion occupies each bowl-shaped cavity (two per molecule) created by the ligand architecture and each anion makes a three point hydrogen bond with the protons of the μ3–OH bridging ligands. A fifth anion is associated with the oxidized cluster 2.2, but remains outside the cavities and does not act as a hydrogen bond acceptor. The donor-acceptor (D···A) distances between the triflate anions and the μ3–OH of 2.2 are 2.855(3), 2.870(3) and 2.942(3) Å (dashed lines, Figure 2.1), whereas the

![Figure 2.3](image)

**Figure 2.3** (a) ESI mass spectrum of 2.1 in acetonitrile. Green is the observed spectrum and red is the simulated spectrum for the indicated cationic complex. (b) ESI mass spectrum of 2.2 in acetonitrile. Blue is the observed spectrum and red is the simulated spectrum for the indicated cationic complex.
interaction with 2.1 is much weaker as indicated by the significantly longer D⋯A distances; 3.005(3), 3.043(4), and 3.063(3) Å (dotted lines, Figure 2.1).

Three different analyses were performed to understand the interaction of triflate with 2.1 and 2.2 in solution. First, ESI mass spectra were examined to assess the stability of anion–bound complexes in acetonitrile solutions. Figure 2.3 shows the observed and calculated mass spectra for 2.1 and 2.2 in acetonitrile. The most intense signals in the spectrum of 2.1 appears at 758.54 m/z, corresponding to the anion-bare cluster, Co7(OH)6(L)62+, whereas in the spectrum of 2.2, the strongest signal observed appears at 823.97 m/z and corresponds to the triflate-bound Co7(OH)6(L)6(OTf)2+. The m/z signature for the anion-bare 2.23+ was observed, but has a 10% relative intensity compared to the anion-bound 2.2OTf2+.

Second, 19F NMR was used to probe the chemical environments of the triflate anions in the clusters. Despite the paramagnetic behavior of 2.1 and 2.2, clear 19F signals were observed (Figure 2.4). At room temperature, the triflate signal for 2.2 is shifted 9.16 ppm upfield of 2.1, which itself is very near to free triflate in an acetonitrile solution of

![Figure 2.4](image-url) 19F NMR spectrum of recorded at 293 K and 282.38 MHz in CD3CN of (a) TBAOTf, (b) 2.1 and (c) 2.2.
The linewidths of both spectra are broadened relative to TBAOTf (3.93 Hz), with a significantly increased broadening in \(2.2\) (27.12 Hz) as compared to \(2.1\) (9.49 Hz). The broadening in \(2.2\) cannot be attributed to paramagnetism alone because it is less paramagnetic than \(2.1\), which shows a sharper linewidth.

Figure 2.5 shows \(^{19}\)F NMR spectra at 500 MHz, in the temperature range indicated of (a) \(2.1\), 8 mM in CD\(_3\)CN and (b) \(2.2\), 10 mM in CD\(_3\)CN. Spectra were referenced to TBAOTf in CD\(_3\)CN.

TBAOTf. The linewidths of both spectra are broadened relative to TBAOTf (3.93 Hz), with a significantly increased broadening in \(2.2\) (27.12 Hz) as compared to \(2.1\) (9.49 Hz). The broadening in \(2.2\) cannot be attributed to paramagnetism alone because it is less paramagnetic than \(2.1\), which shows a sharper linewidth.

Figure 2.5 presents the NMR for samples that were cooled to \(-40\) °C in order to explore the possibility of chemical exchange. With decreasing temperature, an increased broadening of the \(^{19}\)F signal and a downfield shift were observed in \(2.2\), whereas the linewidth for \(2.1\) changes only slightly with no noticeable perturbation of the chemical shift. This is consistent with fast exchange between inequivalent triflate anions in \(2.2\), but not in \(2.1\), and because the shift in \(2.2\) is downfield, towards the signal for “free” triflate, it suggests that two of the three triflate anions are less influenced by the chemical environment of the cluster than the third.
Finally, the O–H stretching energies of 2.1 and 2.2 were analyzed in solution and the solid state by IR spectroscopy. The data are presented in Figure 2.6. The IR spectrum of co–crystals of 2.1 and 2.2 contains peaks at 3580 cm$^{-1}$ and 3462 cm$^{-1}$, assigned to 2.1 and 2.2, respectively. These stretches match well with independent solid samples of 2.1 and 2.2. In solution, the large separation between the major peaks is maintained and even increases slightly due to an approximate 60 cm$^{-1}$ shift to lower energy in the spectrum of 2.2. In both solution spectra, the presence of high energy shoulders suggests asymmetric hydrogen bonding.

**Figure 2.6** IR spectra in the O–H stretching region. (a) Comparison between 2.1/2.2 co–crystals and solid powder sample of 2.1 and 2.2. (b) Comparison between solid powder samples and solution samples of 2.1 (8 mM) and 2.2 (10 mM) in CD$_3$CN.
The magnetic properties of 2.2 were investigated in the solid state by SQUID magnetometry and in solution by variable temperature Evans method. The data are presented in Figure 2.7. The magnetism of the perchlorate salt of 2.1 was previously reported. The room temperature $\chi_M T$ value for 2.2 was 16.3 cm$^3$ mol$^{-1}$ K as measured by the Evans method; this is approximately 4.5 cm$^3$ mol$^{-1}$ K less than that measured for 2.1. The slow increase in $\chi_M T$ with decreasing temperature is suggestive of weak intramolecular ferromagnetic exchange between Co(II) ions, and is consistent with data from 2.1 and other disc–like heptanuclear clusters. Importantly, these magnetic data indicates that Co(1) in 2.2 has a low-spin electronic structure and that a spin equilibrium, which is known for Co(III) ions in weak oxygen–atom ligand fields, is not operable within this temperature range.

Figure 2.7 Variable temperature magnetic susceptibility plot for 2.2 in the solid state (●) at 1000 Oe and in a CD$_3$CN solution (○) using the Evans method.
2.2.2 Self–Exchange Kinetics.

The rate of electron transfer between 2.1* and 2.2 in MeCN with no added electrolyte was studied over the temperature range of 40 to 70 ºC. To ensure that only electron transfer and not ligand substitution resulted in the productive transfer of the label from 2.1* to 2.2*, control experiments were performed in which 2.1* and 2.2* were separately treated with 2.3 for 18 h at 50 ºC. Co(II) and Zn(II) ions have similarly fast ligand exchange rates, so the lack of ligand scrambling between 2.3 and 2.1* or 2.2*, provided assurance that within the temperature range of the study, only electron transfer was responsible for the apparent transfer of L*.

Representative traces of the raw NMR data at 40 ºC and the subsequent monoexponential fit are shown in Figure 2.8. The average of two kinetic runs at this temperature resulted in a $k_{\text{obs}} = 1.53 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ at 38 mM total concentration of triflate, $[\text{OTf}]_{\text{total}}$. As the reaction temperature was raised, the rate constant increased to $2.93 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$ at 70 ºC and 21 mM $[\text{OTf}]_{\text{total}}$. The temperature dependent data, plotted in the Eyring form, are presented in Figure 2.9. The data exhibit excellent linearity and a least–squares fit produces a $R^2 = 0.99$ with a slope of $12200 \pm 300$ K and intercept of $27 \pm 1 \ln(\text{M}^{-1} \text{s}^{-1})$. 

Figure 2.8 (a) Representative stacked plot of the increase in $^1$H methyl iminium signal during a kinetics measurement at 40 ºC in MeCN, $[C_1] = 8.65 \text{mM}$ and $[C_2] = 6.21 \text{mM}$. (b) The integration of the signal versus time and subsequent monoexponential fit to furnish $\tau = 43100 \pm 900 \text{s}$. 

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The anion dependence on $k_{\text{obs}}$ was probed at 60 °C. Due to solubility concerns, the highest concentration of TBAOTf that could be added was 60 mM. An inhibitory effect of the anion was observed; $k_{\text{obs}}$ decreased by a factor of two (inset, Figure 2.9) as the total concentration of triflate was raised from 22 mM to 85 mM.

![Figure 2.9](image)

**Figure 2.9** Temperature dependence of the observed rate constant in MeCN, plotted in the Eyring form, $\ln(k_{\text{obs}}/T)$ vs. $1/T$. The average $[\text{OTf}]_{\text{Total}} = 30 \pm 10$ mM. The linear fit yields a slope of $-12200 \pm 300$ K and intercept of $27 \pm 1 \ln(M^{-1} \text{s}^{-1})$. (Inset) Dependence of $k_{\text{obs}}$ at 60 °C on the concentration of triflate from all sources, $[\text{OTf}]_{\text{Total}} = [\text{OTf}]_1 + [\text{OTf}]_2 + [\text{OTf}]_{\text{TBAOTf}}$. The line is presented merely as a guide.

### 2.3 Discussion

#### 2.3.1 Electron Transfer Rate Calculations

The theoretical self–exchange rate constant at 40 °C was calculated using semiclassical Marcus theory for comparison to the experimental value:\(^4,^8\)

$$k_{\text{ET}} = K_A v_0 \kappa_{\text{el}} \exp \left[ -\frac{[\Delta G^*_{\text{out}} + \Delta G^*_{\text{in}}(T)]}{RT} \right]$$  \hspace{1cm} (1)

$$K_A = 4\pi N r^2 \delta r \exp \left( -\frac{w(r)}{RT} \right)$$  \hspace{1cm} (2)
Initially, we assume that the electron transfer is adiabatic and thus the electronic factor, $\kappa_{el} = 1$. As Sutin has emphasized, though Co(II)|Co(III) exchanges are formally spin forbidden and therefore should be inherently nonadiabatic, comparisons of observed rate constants to calculated rate constants do not allow for any special nonadiabaticity. The nuclear tunneling correction is applied because of the large change in the bond distance at the Co(1) atom. Even at high temperatures, this correction can result in a significant decrease in the free energy of inner sphere reorganization, $\sim 4$ kJ/mol for $\Delta d_0 = 0.17$ Å. The crystal structure of 2.1 co–crystallized with 2.2 is used as a representation of the reactants in a precursor complex and, conveniently, many input parameters for eqs (1) – (6) are deduced from it directly. To begin, we assume that only the largest bond distance changes, Co(1)–O(1) and Co(2)–O(1), in Table 2.1 play a dominant role in the inner sphere reorganization energy. The average breathing frequencies, $v_i$, are estimated from vibrational data to be 425 cm$^{-1}$ and 366 cm$^{-1}$, respectively (Figure 2.10). Using these values, the inner sphere reorganization energy was calculated using eq (4), $\Delta G_{in}^*(T) = 50.9$ kJ/mol. The hard sphere radii of the reactants, $a_2$ and $a_3$, and the center-to-center distance, $r$, were measured for nearest neighbor pairs and found to be, $a_2 = a_3 = 6.6$ Å and $r = 12.2$ Å.
Å (see section 2.5.9 for details on the calculations of a₂ and a₃). Using these metrics and known physical constants for acetonitrile, ΔGₘₐₜ *= 12.7 kJ/mol is evaluated from eq (5). This value is ~2 times smaller than many Co(II)|Co(III) couples, traditionally studied in water, owing to the lower dielectric constant for acetonitrile and the large sizes of 2.1 and 2.2.²²

The equilibrium constant for precursor complex is given by eq (2) and includes a work contribution for the formation of the precursor complex, which is dependent on ionic strength. The importance of the work term is illuminated by the dependence of the observed rate constant on electrolyte concentration, the data for which is presented in the inset of Figure 2.9. Debye-Hückel theory predicts that for similarly charged species, increasing the ionic strength will increase the rate constant by decreasing the magnitude of the work term.²³ Also, the rate constant for electron transfer may be further influenced to the extent that higher ionic strength may increase the ion pairing of reactants and their counter ions. Indeed, self-exchange and cross-exchange studies in acetonitrile have shown the expected increase in rate constant with increasing electrolyte concentration when the reactants are

**Figure 2.10** Far IR spectra of (a) 2.1 synthesized with natural water (-----) and ¹⁸O enriched water (——). The indicated shifts of ν₁₈/ν₁₆ = 0.96 are consistent with a Hooke’s Law analysis. (b) 2.1 (-----) and 2.2 (——), the arrows indicate vibrational changes used for calculating the inner sphere reorganizational energy.
of like charge.\textsuperscript{24,25} Since electrolyte had an inhibitory effect in this study, it is reasonable to assume that at the concentrations employed, there is sufficient ion pairing to make the work term negligible or at least small enough that other processes, which are inversely dependent on anion, are more influential. With the assumption that \( w(r) \) is negligible, the equilibrium constant was calculated, \( K_A = 0.9 \text{ M}^{-1} \). If the work term is included, the equilibrium constant is reduced by a factor of 14 to \( K_A = 0.06 \text{ M}^{-1} \), i.e., when assuming no ion pairing and an ionic strength of \( \mu = 68 \text{ mM} \) (the average of the 40 °C trials). The rate constant at 40 °C is \( k_{SE}(\text{calc}) = 3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \) using \( K_A = 0.9 \text{ M}^{-1} \), the reorganizational energies mentioned previously, and a nuclear vibrational frequency (\( \nu_n = 10^{13} \text{ s}^{-1} \) from eq (6)). This calculated rate constant is five orders of magnitude higher than the observed value. Even with a large work term included, \( k_{SE}(\text{calc}) = 3 \times 10^1 \text{ M}^{-1} \text{ s}^{-1} \). Thus, \( k_{SE}(\text{obs}) \) is considerably smaller than what is expected for any experimental condition invoked for an adiabatic electron transfer.

### 2.3.2 Evidence for the Mechanism of Hexaaqua Self-Exchange ET.

A comparison of the observed \( k_{SE} \) for 2.1|2.2 self-exchange and Co(OH\(_2\))\(_6^{3+/2+}\) relative to those calculated by Marcus theory provides insight into the mechanism of Co(II)|Co(III) self-exchange. Compounds 2.1 and 2.2 retain the hexaaqua-like O-atom ligand field, but unlike Co(OH\(_2\))\(_6^{3+/2+}\), these compounds possess a secondary coordination structure that precludes electron transfer by an inner–sphere pathway. Conversely, 2.1 and 2.2 are electronically similar to Co(OH\(_2\))\(_6^{3+/2+}\) owing to similar ligand fields and therefore the participation of excited states, if they are important to Co(II)|Co(III) self-exchange, will prevail in either system. In this case, both 2.1 and 2.2 and Co(OH\(_2\))\(_6^{3+/2+}\) would be expected to have inflated \( k_{SE} \) relative to that predicted by Marcus theory. Conversely, \( k_{SE} \) of 2.1/2.2 should be slower than a Marcus-predicted rate constant owing to the steric clashing of the cluster cores (and attendant six chelating ligands) and the coordinative saturation of Co(1) whereas \( k_{SE} \) of Co(OH\(_2\))\(_6^{3+/2+}\) should be greater than a Marcus-predicted
rate constant owing to the facility of inner-sphere complex formation, as originally proposed by Endicott and co-workers.\(^7\)

In assessing the participation of excited states, and in particular, the high-spin \(^5\)T\(_2\) excited state in Co(II)|Co(III) self-exchange electron transfer, a ligand field analysis is useful. Because the ligand environments of the periphery Co(II) ions are similar in both 2.1 to 2.2, the absorption profiles in the visible range are nearly identical for the two molecules (Figure 2.11). Thus, the d-d transitions of the Co(III) atom in 2.2 are obscured by those of the neighboring Co(II) atoms and thus identification of the \(^5\)T\(_2\) excited state in

![Figure 2.11 Visible and near-IR spectra of 2.1 (---) and 2.2 (--), recorded at 293 K in CH\(_3\)CN.](image)

**Figure 2.11** Visible and near-IR spectra of 2.1 (---) and 2.2 (--), recorded at 293 K in CH\(_3\)CN.

2.2 is obstructed. Notwithstanding, the structural metrics of 2.2 support the conjecture of a weak, and likely weaker, ligand field for Co(III) in 2.2 than that for Co(III) residing in a hexaaqua environment. The Co(II) \(\rightarrow\) Co(III) bond distance contraction of 0.174 Å (Table 2.1) is much smaller than the 0.21 Å contraction seen for the hexaaqua complex.\(^{26}\) Furthermore, the interaction of the Co(1) atoms with the \(\mu_3\text{–OH}\) ligands will polarize electron density away from putative Co(2) bonding interactions. A similar interaction between La and O ions occurs in the solid-state material, LaCoO\(_3\).\(^{27}\) In LaCoO\(_3\), this
polarization stabilizes the intermediate and high-spin excited states of the Co(III) ion with respect to the low-spin ground state, resulting in a non-zero bulk magnetic moment at temperatures above 100 K. Together, the longer metal ligand bonds and polarization effect suggest that a weaker ligand field is expected for Co(III) in 2.2 and correspondingly the \(^5T_2\) excited state should be to lower-energy than in Co(OH\(_2\))\(^6\text{3+}\). Though the involvement of a high-spin excited state of 2.2 would be more probable than for Co(OH\(_2\))\(^6\text{3+}\), the \(k_{\text{SE}}\) for 2.1\|2.2 self-exchange is exceptionally small, indicating that the excited state does not mediate electron transfer. In this regard, these results support the notion that a water-bridging mechanism is operable and explains the very high Co(II)|Co(III) self-exchange rates of Co(OH\(_2\))\(^{3+/2+}\).

### 2.3.3 Origins of Slow Electron Transfer.

While the water-bridged mechanism explains the fast Co(II)|Co(III) self-exchange rate of Co(OH\(_2\))\(^{3+/2+}\), it does not account for the exceptionally slow 2.1\|2.2 self-exchange reaction. In the absence of an inner sphere mechanism, Marcus theory predicts a \(k_{\text{SE}}\) that is five orders of magnitude greater than the observed rate constant.

\[
k_{\text{obs}} = \frac{k_B T}{\hbar} \exp \left( \frac{-\Delta H^\dagger}{RT} \right) \exp \left( \frac{\Delta S^\dagger}{R} \right)
\]  

(7)

The temperature dependence of the rate constant provides evidence as to the source of the discrepancy. An analysis of the slope of Figure 2.9 using eq (7) results in an experimental activation enthalpy of 99 ± 1 kJ/mol, which is 35 kJ/mol larger than the value calculated using eqs (4) and (5). This increased enthalpy is more than enough to account for a \(10^5\) difference between the experimental and calculated rate constant. Thus, the discrepancy between \(k_{\text{obs}}\) and \(k_{\text{calc}}\) appears to arise from an underestimation of the enthalpy of activation. With an excellent model of the precursor complex provided by the crystal structure, the activation parameters, \(\Delta G(T)_{\text{in}}\) and \(\Delta G_{\text{out}}\), are calculated with good assurance. However, a larger enthalpy of activation is expected if electron transfer is coupled to movement of a hydrogen-bonded triflate anion. The inhibitory effect of counterion
movement on ET rate constants has been recognized for both intra- and intermolecular ET in organic solvents.\textsuperscript{30,31} Given that the crystal structures imply a preference for triflate association to \textbf{2.2}\textsuperscript{3+} and \textsuperscript{19}F NMR, ESI-MS, and IR data of \textbf{2.2} indicate anion association is preserved in solution, it is expected that the dominant solution species for the oxidized cluster is \([\textbf{2.2OTf}]^{2+}\). A model for self-exchange electron transfer between the thermodynamically stable solution species that accounts for anion association is depicted in Scheme 2.1. Whereas \textsuperscript{19}F NMR indicates fast triflate exchange on the NMR timescale, electron transfer is slow on this timescale. The electron transfer step is therefore expected to be rate limiting in all cases. For this reason, we consider only anion dynamics that precedes or accompanies electron transfer, thus simplifying the kinetic analysis.\textsuperscript{32}

The relevant rate expression for ET is:

\[
R_{ET} = k_{ET1}[\textbf{2. 1}\textsuperscript{2+}][\textbf{2. 2}\textsuperscript{3+}] + k_{ET2}[\textbf{2. 2}\textsuperscript{2+}][\textbf{2. 1}] + k_{ET3}[\textbf{2. 1}\textsuperscript{2+}][\textbf{2. 2OTf}\textsuperscript{2+}]
\]

\textbf{Scheme 2.1 Self-exchange ET Mechanism}
where $C_{2.1} = [2.1] + [2.1^*]$ and $C_{2.2} = [2.2] + [2.2^*]$ and acknowledging $K_{D2} \ll [OTf]_{\text{free}}$, then the observed rate constant becomes,

$$k_{\text{obs}} = k_{ET1} \frac{K_{D2}}{[OTf]_{\text{free}}} + k_{ET2} + k_{ET3}$$

(9)

All three terms of eq (9) are expected to give observed enthalpies of activation that exceed that predicted from Marcus Theory, albeit, for difference reasons. Electron transfer at the nuclear configuration of the precursor complex $[2.1-2.2OTf]^{4+}$, $k_{ET2}$, will be thermodynamically uphill by the value determined by the ratio of the anion dissociation constants:

$$\Delta G_{ET2}^{\circ} = -RT \ln \frac{K_{D2}}{K_{D1}}$$

(10)

which, since experimental data suggests $K_{D2}/K_{D1} \ll 1$ is expected to be significant. Electron transfer that is concerted with anion transfer, $k_{ET3}$, will be thermoneutral, but will have an increased reorganizational energy due to the movement of the anion, eq (11).

$$\Delta G_{ET3}^{\ddagger} = \Delta G_{\text{anion}}^{\circ} + \Delta G_{\text{in}}^{\circ} + \Delta G_{\text{out}}^{\circ}$$

(11)

Finally, electron transfer that follows a fast anion preequilibrium, $k_{ET1}$, will result in a higher observed enthalpy of activation because the measured value will encompass the enthalpic component of both steps, anion dissociation and electron transfer, eq (12).

$$\Delta G^{\ddagger} = \Delta G_{ET1}^{\circ} + \Delta G_{K_{D2}}^{\circ}$$

(12)

However, only this first term of eq (9) can account for the observed decrease in $k_{\text{obs}}$ with increasing triflate concentration. Thus, at the concentrations explored, the pathway that accounts for the observed scrambling of the deuterium label is a facile anion dissociation
pre-equilibrium from $\text{2.2OTf}^{2+}$ to give precursor complex for which rate limiting electron transfer proceeds with a $\Delta G^\circ_{\text{ET1}} = 0$ (Scheme 2.2).

Since the electron transfer is between spin-orthogonal cobalt atoms that are separated by 12.2 Å, the electronic factor, $\kappa_{\text{el}}$, is expected to be much less than 1, i.e., the electron transfer should be nonadiabatic. However, as has been observed with other Co(II)|Co(III) couples, the slow observed rate constant measured in this study can be accounted for by a large enthalpy of activation. The experimentally derived preexponential term, assuming no contribution due to entropy from inner or outer reorganization energies, is,

$$K_A v_n \kappa_{\text{el}} = \frac{k_{\text{obs}}}{\exp\left(-\frac{\Delta H^\dagger}{RT}\right)} (@313K) = 5 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$$

which is within an order of magnitude of the calculated preexponential term assuming $\kappa_{\text{el}} = 1$. The effect of nonadiabaticity may be slight or hidden by a counter balancing of a positive entropy component, which could be expected for a dissociation mechanism.
Anion mediated electron transfer provides a molecular basis for the observed inverse first order dependence on buffer in the mechanism of Co-OEC catalyst self-assembly. The electrokinetic model for Co-OEC nucleation indicates that methyl phosphonate (MeP) inhibits film growth\(^2\). We originally suspected that this anion dependence found its origin in an inner-sphere ligand substitution, where the MePO\(_3^{2-}\) anion dissociates from the growing Co-OEC cluster prior to a rate determining adsorption of a cobalt atom from solution. However, the studies described herein suggest that the anion may also modulate the kinetics of electron transfer via hydrogen bonding, and this new perspective, in combination with model studies discussed in Chapter 1, have led to a revision of the proposed mechanism for Co-OEC deposition.

The original proposed mechanism, depicted in Figure 1.9 of Chapter 1, is consistent with an experimental rate law, distinguished by an inverse dependence on the MePO\(_3^{2-}\) anion and a potential-dependent equilibrium ET. However, it is known that substitution reactions at Co(III) centers are very slow due to the inert nature of d\(^6\), low spin complexes,\(^34\) and therefore, it is unlikely that this type of ligand dissociation could exist in a fast equilibrium step. A more plausible explanation for the equilibrium dissociation of the buffer anion, which is consistent with the model studies above, involves a hydrogen-bonded MePO\(_3^{2-}\) species, which rapidly associates and dissociates with surface edge site of the Co-OEC. Once the anion dissociates, a site is opened for solution-based Co\(^{2+}\) to bind before subsequent oxidation to Co(III).

The precise mechanism by which Co(II) is oxidized to Co(III) can now also be reevaluated. It is now known that charge transport to the edge of the growing films must occur via an ET mechanism that involved charge hopping between Co-OEC clusters.\(^35\) It was initially proposed that Co(II) in solution was directly oxidized by the underlying conducting electrode. Rather, a film mediated ET mechanism is more likely because film growth proceeds efficiently even when the thickness of the film exceeds length scales that could allow electrons to tunnel from the solution directly to the electrode, i.e. 5-10 nm. For
example, the steady-state Tafel data, which forms the basis of the rate law for deposition, eq. 3 of chapter 1, were collected using predeposited films of ~ 70 nm (10 mC/cm²), and over the of course those experiments, the films continued to grow without any change in the observed Tafel slope, which would have indicated a passivation of the rapid equilibrium ET.

The nature of cobalt species in the films that mediates the ET is informed by model studies as well as previously discussed spectroscopic measurements of the Co-OEC films. Since the hopping mechanism can be thought of as a self-exchange reaction between small domains in the Co-OEC films, self-exchange studies with model complexes, such as the cubanes, 1.1-H⁺ and 1.2, discussed in Chapter 1 and the Co7 clusters, 2.1 and 2.2, discussed here provide useful comparisons. Since the measured self-exchange rate constant between 2.1 and 2.2 is slow, it is unlikely that an exchange between Co(II) and Co(III) in an oxidic ligand field could be fast enough to exist as electrochemical preequilibrium. On the other hand, a self-exchange between Co(III) and Co(IV) species can be quite fast as demonstrated in the study of PCET self-exchange between 1.1-H⁺ and 1.2. Furthermore, the EPR studies on the Co-OEC films demonstrated that at 1.03 V (vs. NHE) a signal for Co(IV) can be observed.36 This potential is only 100–200 mV more positive than the potential region investigated by Tafel analysis for the deposition mechanism. Therefore, it is reasonable that the minor equilibrium ET leads to the oxidation of the Co(III) film to a minor Co(IV) species—the same species as the resting state of the Co-OEC catalyst during turnover—that then diffuses in a series of self-exchange ET events to the surface of film.
This diffusion process is analogous to that of the active form of the Co-OEC (intermediate $\text{Co}^{2\text{IV}}$) but instead involves a lower oxidation state of the film. A revised model of mechanism of Co-OEC film grow can now be presented in Scheme 2.3.

The revised deposition mechanism is now summarized. The hydrogen-bonded $\text{MePO}_3^{2-}$ makes the edge site Co(III) atoms more susceptible to oxidation since it allows the inner-sphere hydroxide ligands to donating more electron density into orbitals of the metal. The oxidation of the exposed Co(III) to Co(IV) is coupled to a deprotonation in a PCET event, while in solution, a $\text{Co(OH}_2\text{)}_{6}^{2+}$ species is in minor equilibrium with its deprotonated form, $\text{CoOH(OH}_2\text{)}_{5}^{1+}$. Following the rapid dissociation of $\text{MePO}_3\text{H}^{1-}$, the solution species associates with the surface of the film, likely through an inner-sphere bridging species. A comproportionation ET of the Co(IV) and Co(II) species into two Co(III) species leads to the growth of the film by one cobalt atom.

The rate determining chemical step could involve the binding of the solution species to the film, as originally proposed; however, it is more likely that the “chemical” step defined by the Tafel slope analysis is actually the ET comproportionation. This is predicted to be a slow event since a Co(II) species is being oxidized to Co(III), leading to large changes in bond lengths. Importantly, because this ET does not involve the electrode
directly, its influence on the Tafel slope is indistinguishable from a “chemical” step, which is usually considered to involve the formation or cleavage of chemical bonds.

2.4 Conclusion

In summary, an improved synthesis of disc–shaped heptanuclear cobalt hydroxide model compound has been extended to the preparation of an analogous zinc complex. The one-electron oxidized cobalt compound features a localized Co(III) valency in a weak, oxygen atom ligand field. The self–exchange electron transfer rate constant as measured by isotope exchange reveals an anomalously slow self–exchange electron transfer rate constant as compared to that predicted from semiclassical Marcus theory. The discrepancy in observed and calculated rates supports a charge transfer mechanism that requires anion dissociation from the oxidized cluster before electron transfer can occur. This mechanism sheds light on the inverse dependence of anions in the self-repair mechanism of Co–OECs. Moreover, because H$_2$O cannot directly bridge cobalt centers, owing to the encapsulation of the central Co within the cluster core, the observed results support the contention that the Co(OH$_2$)$_6^{3+/2+}$ self-exchange electron transfer occurs by an inner-sphere mechanism via a bridging water versus the involvement of high-spin excited states of cobalt ion.
2.5 Experimental Methods

2.5.1 General Considerations.

O-vanillin, methylamine (33% wt solution in absolute ethanol), methyl-d$_3$-amine hydrochloride, and triethylamine were purchased from Sigma-Aldrich, CoCl$_2$·6H$_2$O was purchased from Noah Technologies and AgOTf and Zn(OTf)$_2$ were purchased from Strem. Acetonitrile-d$_3$ (1 gram ampoules) was purchased from Cambridge Isotopes Laboratories and $^{18}$O enriched water (>98%) was purchased from Shanghai Research Institute of Chemical Industry. Commercial reagents were used as received. HL (2-iminomethyl-6-methoxy-phenol) was synthesized as described elsewhere.$^{37}$ HL* (2-iminomethyl-d$_3$-6-methoxy-phenol) was synthesized in an analogous manner with the exception that CD$_3$NH$_2$ was produced by the neutralization of CD$_3$NH$_2$·HCl with 1 equiv of triethylamine. Co(OTf)$_2$·(H$_2$O)$_x$ was prepared using a modification of a known procedure.$^{38}$ Salt metathesis was accomplished by mixing CoCl$_2$·6H$_2$O with 2 equiv of AgOTf in deionized water. The AgCl was removed by filtration using Celite on a medium porous frit. The filtrate was concentrated and dried for 24 h in vacuo while agitating with a large stir bar. The resulting pink powder was slightly hydroscopic and therefore stored in a desiccator over CaSO$_4$. The molecular weight of the Co(OTf)$_2$·(H$_2$O)$_x$ was determined by dissolving known masses in deionized H$_2$O and back extracting using $\varepsilon = 4.8$ M$^{-1}$ cm$^{-1}$ at $\lambda_{max} = 510$ nm for Co(H$_2$O)$_6^{2+}$.$^{39}$ The average of three trials gave a molecular weight of 445 g/mol (very near that of Co(OTf)$_2$·5(H$_2$O), 447.15 g/mol). This material was then used to prepare a 0.2 M stock solution in 1:1 CH$_3$CN:H$_2$O. Complexes 2.1 and 2.2 were not significantly moisture or O$_2$ sensitive; therefore, no attempt was made to exclude water or O$_2$ during their syntheses. Nonetheless, once synthesized, 2.1 and 2.2 were stored in a desiccator over CaSO$_4$. Elemental analyses performed by Midwest Microlab.

2.5.2 Preparation of Co$_7$(OH)$_6$(L)$_6$(OTf)$_2$ (2.1).
To 20 mL of a 0.20 M solution of Co(OTf)\textsubscript{2} in 1:1 MeCN:H\textsubscript{2}O (4.0 mmol, 7.0 equiv) was added 20 mL of a 0.17 M solution of HL in MeCN (3.4 mmol, 6.0 equiv). To this was added 943 µL of NEt\textsubscript{3} (6.86 mmol, 12.0 equiv). A deep red solution formed immediately. Slow addition of 5 mL of water induced precipitation of a pink solid. This solid was filtered and washed with 20 mL of 1:3 MeCN:H\textsubscript{2}O, then dried in air. This material was dissolved in 80 mL of MeCN and filtered through paper to remove a minor insoluble impurity. The resulting solution was concentrated and dried in vacuo. Yield: 742 mg of pink solid (0.413 mmol, 72.3 % yield). \textsuperscript{1}H NMR is shown below Figure 2.12 (CD\textsubscript{3}CN, δ, all signals are paramagnetically broadened): 59.58 (6H), 57.20 (18H), 47.29 (6H), 12.97 (6H), −13.13 (18H). HR-ESI-MS (m/z): [M\textsuperscript{2+} – (OTf)\textsubscript{2}] Calcd for C\textsubscript{54}H\textsubscript{66}N\textsubscript{6}O\textsubscript{18}Co\textsubscript{7}, 749.4873; Found, 749.4868. Anal. Calcd. for C\textsubscript{56}H\textsubscript{68}N\textsubscript{6}O\textsubscript{24}S\textsubscript{2}F\textsubscript{6}Co\textsubscript{7}: C, 37.41; H, 3.70; N, 4.67. Found C, 37.15; H, 3.69; N, 4.44.

![Figure 2.12](image-url) \textsuperscript{1}H NMR spectrum of 2.1, recorded at 293 K and 500 MHz in CD\textsubscript{3}CN.
2.5.3 Preparation of $\text{Co}_7(\text{OH})_6(\text{L}^*)_6(\text{OTf})_2$ (2.1*).

The labeled complex was prepared in the same manner as 2.1, but at half scale, using HL* in place of HL. Yield: 343.1 mg of pink solid (0.1889 mmol, 66.53%). $^1$H NMR is shown below in Figure 2.13 (CD$_3$CN, δ, all signals are paramagnetically broadened): 59.92 (6H), 57.38 (18H), 47.48 (6H), 13.06 (6H). HR-ESI-MS (m/z): [M$^{2+}$ – (OTf)$_2$] Calcd (C$_{54}$H$_{48}$D$_{18}$N$_6$O$_{18}$Co) 758.5438; found 758.5414. Anal. Calcd. for C$_{56}$H$_{48}$D$_{18}$N$_6$O$_{24}$S$_2$F$_6$-Co$_7$: C, 37.04; H, 3.66; N, 4.63. Found C, 37.34; H, 3.72; N, 4.70.

![Figure 2.13](image_url)

**Figure 2.13** $^1$H NMR spectrum of 2.1*, recorded at 293 K and 500 MHz in CD$_3$CN. The circle highlights the missing proteo peak and indicates complete deuteration at the methyl imine position.

2.5.4 Preparation of $\text{Co}_7(\text{OH})_6(\text{L})_6(\text{OTf})_3$ (2.2).

To a solution of 2.1 (172.6 mg, 0.9600 mmol) in 10 mL of nitromethane was added AgOTf (24.7 mg, 0.0960 mmol) in 630 µL of nitromethane. The mixture was stirred overnight at 40 ºC, by which time a silver mirror had formed. The solution was filtered through a combination of Celite and glass wool to remove finely divided Ag$^0$, then
concentrated and dried in vacuo. Yield: 180.8 mg of brown solid (0.09287 mmol, 96.74%).

$^1$H NMR is shown below in Figure 2.14 (CD$_3$CN, $\delta$, all signals are paramagnetically
broadened): 70.98 (18H), 60.55 (6H), 55.08 (6H), 20.91 (18H), 10.67 (6H). HR-ESI-MS
(m/z): [M$^{2+}$– (OTf)] Calcd for C$_{55}$H$_{66}$N$_6$O$_{21}$SF$_3$Co$_7$, 823.9639; Found, 823.9607. Anal.
Calcd. for C$_{57}$H$_{66}$N$_6$O$_{27}$S$_3$F$_9$Co$_7$: C, 35.16; H, 3.42; N, 4.32. Found C, 35.24; H, 3.43; N,
4.40.

Figure 2.14 $^1$H NMR spectrum of 2.2, recorded at 293 K and 500 MHz in CD$_3$CN.

2.5.5 Preparation of Zn$_7$(OH)$_6$(L)$_6$(OTf)$_2$ (2.3).

3 was prepared in an analogous fashion to 2.1, replacing Co(OTf)$_2$ with Zn(OTf)$_2$
but at a 15% scale. Yield: 122.6 mg of pale yellow solid (0.06647 mmol, 77.55%). $^1$H
NMR is shown below in Figure 2.15 (CD$_3$CN, $\delta$): 8.295 (6H, d), 7.025 (6H, dd), 6.95 (6H,
dd), 6.66 (6H, t), 3.63 (18H, s), 3.31 (18H, d) 1.55 (6H, s). HR-ESI-MS (m/z): [M$^{2+}$–

2.5.6 Physical Measurements.

NMR spectra were recorded at the MIT Department of Chemistry Instrumentation Facility on a Varian Inova-500 NMR Spectrometer. ¹H NMR spectra were referenced to the residual proteo solvent resonances. ¹⁹F NMR spectra were referenced to CFC₁₃. Vis-NIR spectra were recorded at 293 K and samples were prepared in air using acetonitrile previously dried by passage through an alumina column under argon. Extinction coefficients were determined by averaging spectra from nine individually massed samples. IR spectra were recorded on PerkinElmer Spectrum 400 FT-IR/FT-FIR Spectrometer. Solid samples were acquired using a Pike Technologies GladiATR attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. Solution IR measurements were made using KBr windows in a semi-permanent liquid cell.
Magnetic measurements were performed at the MIT Center for Materials Science and Engineering Shared Experimental Facility on a Quantum Design Magnetic Properties Measurement System (MPMS-XL). Solution magnetic measurements were performed using the Evans method in acetonitrile with benzene as the indicator. In both cases, diamagnetic corrections were applied using Pascal’s constants. Mass spectrometry was conducted on a Bruker Daltonics APEXIV 4.7 Tesla FT Ion Cyclotron Resonance Mass Spectrometer using an electrospray ionization source (ESI). Mass spectrometry samples were run in neat acetonitrile and the data were processed using the program mMass Version 4.0.

2.5.7 Kinetics Measurements.

Samples of 2.1* and 2.2 were separately dissolved in 500 µL of acetonitrile-d$_3$ (CD$_3$CN). The total solvent volume was 1 mL to avoid precipitation, which was sometimes observed at lower volumes. The Varian Inova-500 NMR spectrometer was equipped with a variable temperature controller, which maintained the temperature with ± 0.1° of the desired temperature. Once at temperature, the probe was tuned using a 1 mL blank CD$_3$CN sample in a J-Young tube identical to that used for the sample. The solutions of 2.1* and 2.2 were mixed, added to a J-Young tube and firmly sealed. The sample was locked and shimmed, a process which allowed ample time for the sample to equilibrate to the set temperature. The kinetics run was programmed using the array function with a pre-acquisition delay, which was adjusted depending on the temperature. Each FID was composed of sixteen transients with 0.3 sec acquisition time (at) and a first delay (d1) of 4 sec. The spectral window was expanded to include all peaks. All other parameters were the same as a default proton spectrum. Upon completion of the kinetics run, a NMR spectrum of the sample was acquired on a Varian Inova-500 NMR spectrometer with an inverse broadband probe for enhanced proton sensitivity. From this spectrum, an accurate ratio of $C_{2.1}$:$C_{2.2}$, where $C_{2.1} = [2.1] + [2.1^*]$ and $C_{2.2} = [2.2] + [2.2^*]$ was measured by integration of the non-exchanging peaks near 11 ppm. Independent measurements of these peaks with
known amounts of 2.1 and 2.2 confirmed the validity of this method. The sample was then diluted once with CD$_3$CN and a vis-NIR spectrum was recorded to measure the total absorbance at $\lambda_{\text{max}} \sim 666$ nm. From the NMR ratio and the known extinction coefficients of 2.1 and 2.2, the concentrations $C_1$ and $C_2$ were determined by solving two equations with two unknowns. Due to practical experimental restraints, such as time of measurement and solubility, $C_{2.1}$ and $C_{2.2}$ were held within a range of 4–11 mM. The rate of electron transfer, $R_{\text{ET}}$, was measured by applying the MacKay equation,

$$-\ln \left(1 - \frac{[1]_t}{[1]_\infty}\right) = \frac{R_{\text{ET}}(C_{2.1} + C_{2.2})}{C_{2.1} \cdot C_{2.2}} t$$

(15)

to the scrambling of the deuterium labeled between 2.1* and 2.2.$^{41,42}$ The progress of the reaction was conveniently monitored by tracking the increase of the signal from [2.1] at $-10$ ppm. The rate constant was found by fitting the $[2.1]_t$ versus time to a monoexponential function using the program Origin, which resulted in $R^2$ values of 0.985 or greater.

Assuming $R_{\text{ET}} = k_{\text{obs}}C_{2.1}C_{2.2}$, the rate constant is given by,$^{43}$

$$k_{\text{obs}} = \frac{1}{\tau(C_{2.1} + C_{2.2})}.$$  

(16)

2.5.8 X-ray Crystallographic Details.

2.1 and 2.2 co-crystallized from a mixture of 2.1* (15.5 mg) and 2.2 (13.3 mg) in 1 mL of CD$_3$CN, which was left undisturbed at room temperature for 2 weeks. Large block shaped crystals of brown/orange color were collected, and a large single crystal was mounted on a Bruker three circle goniometer platform equipped with an APEX detector. A graphite monochromator was employed for wavelength selection of the Mo Kα radiation ($\lambda = 0.7103$ Å). The data were processed and refined using the program SAINT supplied by Siemens Industrial Automation. Structures were solved using direct methods in SHELXS and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms bound to carbon atoms were placed in calculated positions using the standard riding model and refined isotropically. The oxygen-bonded hydrogen atoms were located in the
difference map and distances were restrained to 0.84 Å. The isotropic displacement parameters of these hydrogen atoms were fixed to 1.2 times the U value of the oxygen atoms to which they were bonded. All non-hydrogen atoms were refined anisotropically. The structure contained a disordered triflate anion and acetonitrile solvate molecule, which occupied the same space adjacent to an inversion center. This disorder was satisfactorily modeled using the Part –1 and Part –2 commands and a site occupancy factor of 0.5. The 1,2-distances and 1,3-distances of the disordered molecules were restrained to be similar using the SAME command, and the rigid bond restraints SIMU and DELU were applied. Hydrogen bonding parameters were calculated using the HTAB command. Unit cell parameters, morphology, and solution statistics for the structures are summarized in Table 2.2. All thermal ellipsoid plots are drawn at the 50% probability level with carbon-bound hydrogen atoms and solvent molecules omitted for clarity.

2.5.9 Electron Transfer Calculation Details

The second order rate constant for self-exchange electron transfer, \( k_{ET} \) is given by,

\[
k_{ET} = K_A u_n \kappa_{el} \kappa_n
\]

where \( K_A \) is the equilibrium constant for the formation of the precursor complex, \( u_n \) is the nuclear vibrational frequency, \( \kappa_{el} \) is the electronic transmission coefficient, and \( \kappa_n \) is the nuclear factor. \( K_A \) can be expressed as,

\[
K_A = 4\pi N r^2 \delta r \exp \left( -\frac{w(r)}{RT} \right)
\]

\[
w(r) = \frac{Nz_2z_3e^2 \exp[\beta(\sigma - r)\sqrt{\mu}]}{4\pi \varepsilon_0 \varepsilon_r r(1 + \beta r \sqrt{\mu})}
\]

where \( N \) is Avogadro’s number (\( \text{mol}^{-1} \)) and \( \mu \) is the ionic strength (M). \( w(r) \) (kJ/mol) is the work required to bring the reactants together in the precursor complex at a separation
distance $r$ between the reactants. This distance was measured to be 12.2 Å from the crystal structure of 2.1 cocrystallized with 2.2, Figure 2.16.

$\delta r$ is the reaction thickness and is taken to be 0.8 Å, as is customary. $\sigma$ is the hard-sphere radius of the reactant $a_2$ (or $a_3$) plus the radius of the main ion of opposite charge. In this study, the hard-sphere radii were calculated from the geometric mean using the follow equation:

$$a_{2 \ or \ 3} = \left[ (a_x + \frac{1.1}{\cos \theta_x}) \times (a_y + \frac{1.1}{\cos \theta_y}) \times (a_z + \frac{1.1}{\cos \theta_z}) \right]^{\frac{1}{3}} \text{Å}$$

where the distances, $a_x$, $a_y$, and $a_z$, were measured from the center cobalt atom, Co(1) to the centroid of three planes as shown in Figures 2.17.
The value of 1.1 Å is the van der Waals radius of the hydrogen atom, and the angles, θ, are between the relevant plane’s normal vector and Co(1)—centroid vector. Using this equation, the radii are found to be \( a_2 = a_3 = 6.6 \) Å. The radius of the triflate anion was determined to be 1.9 Å as measured from the crystal structure. Thus \( \sigma = 8.5 \) Å. \( \varepsilon_r \) is the static dielectric constant of a given medium at 293 K. The term \( 4\pi\varepsilon_0 \) is the fundamental constant of vacuum permittivity. The dielectric constant is adjusted for temperature using the following equation:

\[
\varepsilon_{t'} = \varepsilon_t - \left(-\frac{d\varepsilon}{dt}\right)(t' - t)
\]

where \(-\frac{d\varepsilon}{dt} = 0.160,^3\) and \(t'\) is the temperature of interest. In this study, \(t' = 313\) K and \(\varepsilon_{t'} = 34.3\). The term for \(\beta\) is given by,

\[
\beta = \left(\frac{8\pi Ne^2}{4\pi\varepsilon_0\varepsilon_r k_B T}\right)^{1/2}
\]
is related to the strength of the ionic atmosphere in a given medium and at a given temperature. As given, it has units of $\sqrt{(m/mol)}$, which, using conversion factors from dimensional analysis, is the same as $m^{-1}\sqrt{M}^{-1}$. The other terms in the work expression are Avogadro’s number, $N$, the ionic strength, $\mu$, and the charges of the reactants, $z$ (the subscripts of 2 and 3 are due to the fact that traditionally the charges on the metal centers were +2 and +3).

The nuclear factor, $\kappa_n$, is defined as follows:

$$\kappa_n = \Gamma_n \exp \left[ -\frac{\Delta G_{out}^* + \Delta G_{in}^*}{RT} \right]$$

$$\Gamma_n = \exp \left[ \frac{\Delta G_{in}^* - \Delta G_{in}^*(T)}{RT} \right]$$

$$\kappa_n = \exp \left[ -\frac{\Delta G_{out}^* + \Delta G_{in}^*(T)}{RT} \right]$$

The nuclear tunneling factor, $\Gamma_n$, is important for all electron transfers at low temperatures, but it can have a significant effect even at room temperature when the change in bond lengths is large, as it is for Co(II)/Co(III) couples.

The inner sphere reorganizational energy, $\Delta G_{in}^*$, is calculated as follows:

$$\Delta G_{in}^*(T) = \frac{N}{2} \sum f_i \left( \frac{\Delta d_0}{2} \right)^2 \frac{4kT}{\hbar \nu_i} \tanh \frac{\hbar \nu_i}{4kT}$$

where the average force constant, $f_i$, is

$$f_i = 4\pi^2 \nu_i^2 c^2 m_L$$

and the average breathing frequency, $\nu_i$, is given by

$$\nu_i = \left( \frac{2\nu_2^2 \nu_3^2}{\nu_2^2 + \nu_3^2} \right)^{1/2}$$
where $\Delta d_0$ is the change in equilibrium bond lengths and $m_L$ is the mass of the ligand, 17.007 amu for an OH moiety. The input energies $\nu_2$ and $\nu_3$ come from the far-IR spectra of 2.1 and 2.2 (Figure 2.10). The summation is over all bonds in the precursor complex, so for octahedral complexes the summation is over 12 bonds, 6 bonds $\times$ 2 molecules.

The outer-sphere reorganizational energy, $\Delta G_{out}^*$, is given by

$$\Delta G_{out}^* = \frac{N\Delta q^2}{16\pi\varepsilon_0} \left( \frac{1}{2a_2} + \frac{1}{2a_3} - \frac{1}{r} \right) \left( \frac{1}{n_D^2} - \frac{1}{\varepsilon_r} \right)$$

where, $a_2$ and $a_3$ are the hard-sphere radii of the reactants, and $n_D$ is the refractive index, and $\Delta q$ is the amount of charge past in the electron transfer, equal to e, the elementary charge, in this study.

The remaining terms of the $k_{ET}$ master equation are the nuclear vibrational frequency, $v_n$, and the electronic transmission coefficient, $\kappa_{el}$. There are two limiting cases:

Case 1: Adiabatic electron transfer. In this case, the frequency of electron transfer within the activated complex, $v_{el}$, is much greater than the nuclear vibrational frequency. In other words, every time the vibrational energies within the precursor complex attain enough energy to pass through the intersection region, the electron transfer occurs. In this case $\kappa_{el} = 1$ (the probability of electron transfer is 1) and $v_n\kappa_{el} = v_n$, which is defined as:

$$v_n = \left( \frac{v_{out}^2\Delta G_{out}^* + v_i^2\Delta G_{in}^*}{\Delta G_{out}^* + \Delta G_{in}^*} \right)^{1/2}$$

Because the reorganization energy is this study is dominated by inner sphere modes, the following approximation is valid:\

$$v_n = \left( \frac{v_i^2\Delta G_{in}^*}{\Delta G_{out}^* + \Delta G_{in}^*} \right)^{1/2}$$
The inner sphere reorganizational energy used in this equation is from classical Marcus theory and is given by:

\[ \Delta G_{in}^* = \frac{N}{2} \sum f_i \left( \frac{\Delta d_0}{2} \right)^2 \]

using \( v_{in} = 425 \text{ cm}^{-1} \), \( v_n \) was calculated to be \( 10^{13} \text{ s}^{-1} \).

Case 2: Nonadiabatic electron transfer. In this case, the frequency of electron transfer is much less than the nuclear vibrational frequency, i.e. \( v_{el} \ll v_n \). This means that nuclear coordinates pass through the intersection region many times without the electron transfer occurring. This is because the coupling between the initial and final states is very small, so the system will not jump from one parabola to the other when it passes through this region. It stays on the initial parabola. In this case, the electron transfer coefficient is defined by,

\[ \kappa_{el} = \frac{v_{el}}{v_n} \]

and it follows that \( v_n \kappa_{el} = v_{el} \). The frequency of electron transfer is related to the magnitude of the coupling, \( H_{AB} \), between states as follows:

\[ v_{el} = \frac{2H_{AB}^2}{Nh} \left( \frac{\pi^3}{\Delta G_{out}^* + \Delta G_{in}^*} \right)^{1/2} 4RT \]

When \( H_{AB} = 0.3 \text{ cm}^{-1} \), \( v_{el} = 10^7 \text{ s}^{-1} \) and thus \( \kappa_{el} = 10^{-6} \).
## 2.6 Crystallographic Tables

Table 2.2 Crystal data and structure refinement for $\text{Co}_7(\text{OH})_6(\text{L})_6(\text{OTf})_2 \cdot 5\text{MeCN}$

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---

$^a$ GOF = $\left( \sum_2^2 (\sum \sigma(F_2 - F_2)^2/(n - p)) \right)^{1/2}$ where $n$ is the number of data and $p$ is the number of parameters refined.

$^b$ $R1 = \sum |F_o - |F_e| / \sum |F_o|$.

$^c$ $wR2 = (\sum \sigma(F_2 - F_2)^2)/\sum (\sigma(F_2)^2)^{1/2}$. 

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2.7 References

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Chapter 3 — A Dinuclear Cobalt Complex as a Molecular Mimic of Co-OEC Edge Sites
3.1 Introduction.

During the course of the electron transfer studies, described in Chapter 2, we became cognizant that though the heptanuclear clusters modeled well the large nuclearities of the central core of the Co-OEC, they were poor mimics of the edges of the Co-OEC clusters because they lacked open coordination sites. As indicated in sections 1.4 (Figure 1.8 and Figure 1.9), these open coordination sites were the proposed location of key chemical transformations associated with deposition and water oxidation of activity in the Co-OECs. Therefore, we initiated a research effort with the goal of isolating a Co$_2$(OH)$_4$ diamond core with syn oriented terminal OH ligands, as shown in Scheme 3.1.

**Scheme 3.1 Co-OEC Edge Site**

We envisioned that a molecule that could stabilize this inorganic motif would be of interest for two reasons: 1) given the precedent set by the mononuclear [Co(OH)$_2$(Py5OMe)]$^{2+}$ complex,$^{1,2}$ it was reasonable to assume that within a similar pyridyl-based ligand field, this motif would be active for water oxidation catalysis, and 2) it would be a useful model for understanding the interaction of Co-OEC edge sites with electrolyte species, such as phosphate, P$_i$, and borate, B$_i$. As discussed in Chapter 1, these buffer species are essential components for depositing Co-OECs and must be present in high concentrations to maintain pH during electrolysis.$^3$ Therefore, the role of these buffers beyond just that of proton acceptor, must be considered for a comprehensive understanding of Co-OEC deposition and activity. For example, it is known that the size of the Co-OEC
fragments deposited from Bi are larger than those deposited from Pi, yet the origin of this difference remains uncertain.

In this chapter, we present the isolation of the desired Co₂(OH)₄ diamond core motif within a naphthyridine-based ligand. We show that this molecule is not a water oxidation catalyst, and then perform a detailed comparative investigation of the interactions between Pi and Bi with this edge site mimic (ESM) We show that though the thermodynamic binding constants of Pi and Bi are similar, the kinetics of binding differ by many orders of magnitude due to a facile Lewis acid/Lewis base interaction between boric acid, B(OH)₃, and the ESM. We then demonstrate, as anticipated by the model study, an inverse dependence of [Bi] on the activity of Co-OECs, providing compelling evidence that dinuclear Co₂(OH)₄ edge sites with syn oriented terminal ligands are a crucial coordination motif for water oxidation catalysis by Co-OECs.

3.2 Results

3.2.1 Synthesis and Characterization of [3.1(OH₂)₂][(NO₃)₄]

Realizing the potential of naphthyridine as an ideal backbone for stabilizing a Co₂(OH)₂ diamond motif, we began investigating synthetic pathways for making a polypyridyl ligand with a naphthyridine backbone. We envisioned that this could be accomplished by following a synthetic sequence similar to that used in the synthesis of Py5OMe, Scheme 3.2, the ligand used to stabilize the purported mononuclear cobalt water oxidation catalyst.² Py5OMe was first synthesized and investigated as a ligand for transition metal complexes by Stack & coworkers.⁶,⁷ The key step in the synthesis of Py5OMe is the nucleophilic attack of 2,6 dicarboxyl pyridine with four equivalents of 2-lithiopyridine. This strategy was applied to the naphthyridine analog of 2,6 dicarboxyl pyridine, namely 2,7-dicarboxyl naphthyridine methyl ester, but unfortunately, the electrophilic reactivity of this molecule did not translate as envisioned. A series of nucleophiles were screened, Scheme 3.3, but for all reactions, TLC and ¹H NMR analysis
of the crude material indicated a mixture of products. Based on mass spectrometry data of these mixture, there was evidence that the lithiated heterocycles were directly reducing the naphthyridine, as opposed to reacting nucleophilically.

While this initial synthetic strategy was being investigated, Davenport and Tilley reported the successful synthesis of the ligand, dipyridylethane naphthyridine (DPEN), for stabilizing a dinuclear copper complexes. We envisioned that DPEN could stabilized the desired $\text{Co}_2(\text{OH})_2$ diamond motif; therefore, we adapted their synthesis with a clever one-pot lithiation strategy developed by Ünal et al., which provided DPEN in high yields following a one-pot procedure using 2,7-dichloro-1,8-naphthyridine and commercially available starting materials, Scheme 3.4.

**Scheme 3.2** Py5R Ligand and Proposed Naphthyridine Ligand

![Py5-R and DPN-R structures](image)

**Scheme 3.3** Failed Lithiation Experiments

![Failed lithiation experiments](image)
Later, during the course of the studies described in this chapter, Davenport and Tilley published a study that demonstrated that a similar naphthyridine-based ligand, DPFN, which features a fluorine atom in place of the methyl group in DPEN, could be used to stabilize a dinuclear Co$_2$(OH)$_4$ ESM.$^{10}$ Their studies provided some indication that their molecule could be a water oxidation catalyst, albeit a poor one. They also showed that phosphate anions were prone to binding in a bridging manner across the Co$_2$OH$_2$ diamond core; however, quantitative measurements of the nature of this interaction, as well as, comparisons with other electrolyte species were absent. Subsequently, these authors showed that DPFN could stabilize a variety of diamond core first-row transition metal complexes.$^{11}$

Using the DPEN ligand, the desired Co-OEC ESM, [3.1(OH)$_2$][(NO$_3$)$_4$], was assembled by oxidation of a mixture of 2:1 Co(NO$_3$)$_2$:DPEN with 2 eq. of aqueous peroxide, Scheme 3.5. Elementally pure material could be isolated as a pink solid following precipitation of the nitrate salt from a concentrated aqueous solution with acetone. Single crystals of the complex could be isolated from a pH = 5.5 aqueous solution in the presence
of PF$_6$ anions. The solid-state structure of these crystals is shown in Figure 3.1 and showcases a supramolecular hydrogen bonding interaction within the dimer, [3.1(OH)$_2$(HO)$_3$3.1]$^{6+}$, which forms following an acid-base disproportionation of the mono-deprotonated complex [3.1(OH)(OH$_2$)]$^{3+}$. The Co-O bond lengths (1.90 Å for η-O atoms and 1.89 Å for μ-O atoms) and Co-N bond lengths (1.90 Å for py-N atoms and 1.93 Å for napth-N atoms) are consistent with an oxidation state of Co(III) for all cobalt atoms.
As expected, the compound is diamagnetic as indicated by the well resolved peaks in the $^1\text{H}$ NMR spectrum (see experimental section and Figure 3.2a). The pK$_a$'s of terminal

![NMR spectrum](image)

Figure 3.2 $^1\text{H}$ NMR spectrum in D$_2$O of the aromatic region of [3.1(OH)$_2$]$^{2+}$ (a) pH* = 9.4 with no B$_i$ and (b) pH* = 9.4 with [B$_i$] = 500 mM.

...aqua ligands in [3.1(OH)$_2$][(NO$_3$)$_4$] were measured by titration with NaOH and found to be pK$_{a1}$ = 5.08 and pK$_{a2}$ = 6.75, Figure 3.3, supporting the notion that the mono-deprotonated species, [3.1(OH)(OH$_2$)]$^{3+}$, is stable in pH regime in which the crystals were grown.

The electrochemical properties and possible water oxidation activity of the doubly deprotonated complex, [3.1(OH)$_2$]$^{4+}$, were investigated by cyclic voltammetry (CV). In pH = 9.2 borate buffer, no current beyond background was observed at potentials up to 1.6 V
vs. Ag/AgCl, Figure 3.4 indicating that neither further oxidation of the complex to a Co(IV) species, nor water oxidation catalysis are possible within electrochemical window of this experiment.

Therefore, it can be concluded that [3.1(OH)₂]²⁺ is not active for electrochemically-drive water oxidation catalysis. This may be surprising considering the precedent of water
oxidation catalyzed by the complex $[\text{Co(OH}_2\text{)(Py5OMe)}]^2+$. Though, as will become clearer in Chapter 4, proper catalyst identification is particularly challenging for the study of molecular water oxidation catalysts. We will discuss alternative interpretations of the source of water oxidation catalysis by $[\text{Co(OH}_2\text{)(Py5OMe)}]^2+$ in Chapter 4.

3.2.2 Binding Studies with $\text{B}_i$ and $\text{P}_i$

To rule out possible interference with the borate buffer in the CV experiment mentioned above, $[\text{3.1(OH}_2\text{)}]^4+$ was investigated by $^1\text{H}$ NMR spectroscopy in the presence of $\text{B}_i$, which revealed a new set of peaks in the aromatic region indicating the formation of a new borate bound complex, Figure 3.2b. Inspired by this observation and the knowledge that phosphate could bind in a bridging manner across the dicobalt diamond core, we set out to fully characterize the interaction of these buffer species with our ESM.

The binding interaction with borate was more readily followed using absorption spectroscopy. As shown in Figure 3.5a, the titration of $3.1(\text{OH})_2^{2+}$ with increasing concentrations of $[\text{B}_i]$ at pH = 8.6 and ionic strength, $I = 1$ M, led to a growth of a shoulder

![Figure 3.5](image-url)

Figure 3.5 (a) UV-Vis absorption changes during titration of 250 μM $3.1(\text{OH})_2^{2+}$ with borate buffer at pH = 8.8 and $I = 1$ M. Inset, Benesi-Hildebrand plot with respect to total borate concentration, $[\text{B}_i]_T$. (b) UV-Vis absorption changes during a pH titration of a solution of 250 μM $3.1(\text{OH})_2^{2+}$ and 225 mM $[\text{B}_i]_T$. (c) Color coded schematic of the binding event between the ESM and $\text{B(OH)}_3$. 
at $\lambda = 390$ nm and an increase in intensity of the d-d transition at $\lambda = 499$ nm, with an isosbestic point at $\lambda = 369$ nm. An analysis of the Benesi-Hildebrand (BH) plot of this data, Figure 3.5a inset, resulted in a binding constant with respect to total borate buffer concentration, $[B_i]_T$, of $K_{obs} = 28 \text{ M}^{-1}$. Importantly, when $[B_i]_T$ was held constant at 250 mM, but the pH was gradually increased from 8.8 to 10.5, Figure 3.5b, the spectrum reverts to that of the unbound $3.1\text{(OH)}_2^{2+}$. This indicates that the binding to the ESM occurs with the boric acid component of the buffer, Figure 3.5c, as increasing the pH effectively reduces the concentration of $\text{B(OH)}_3$ in solution. The binding constant extracted from the BH plot could then be reevaluated to consider $\text{B(OH)}_3$ as the sole binding agent. Using the $pK_a = 8.6$ as the appropriate value for the acid dissociation constant of borate at $I = 1 \text{ M}$, a $K_B = 73 \text{ M}^{-1}$ was obtained for the equilibrium binding of $\text{B(OH)}_3$ to the ESM, $3.1\text{(OH)}_2^{2+}$.

When the analogous UV-Vis absorbance experiment was performed at room temperature with $\text{P}_i$ buffer instead of $\text{B}_i$, the changes observed in the spectrum were qualitatively similar, but developed over a much longer timescale. No isosbestic points were observed. As shown in Figure 3.6a, a shoulder near 400 nm appears with time as well as an increase in intensity at $\lambda = 507$ nm, though, even at 70 °C, these absorption features

![Figure 3.6](a) UV-Vis absorption changes of a mixture of 250 $\mu\text{M} \text{3.1(OH)}_2^{2+}$ and 167 mM $\text{KP}_i$ at pH = 8.5 and 70 °C. Inset. Monoexponential fit to the change in absorbance at 390 nm versus time. (b) Linear relationship between $[\text{P}_i]^2$ and first-order rate constant from which third order rate constant is determined. Horizontal line is merely to guide the eye. Error bars are associated with uncertainty in the monoexponential fits.
required ~ 10 hours to reach equilibrium, Figure 3.6a inset. As a comparison, the color changes associated with borate binding appear instantaneous to the eye. The kinetics of the reaction with P\textsubscript{i} were monitored, and with excess P\textsubscript{i} to achieve pseudo first order conditions, the growth at 390 nm could be satisfactorily fit to a mono-exponential equation, Figure 3.6a inset. From a series of experiments with varying [P\textsubscript{i}], a third-order rate constant at 70 °C was determined from the slope of k\textsubscript{obs} vs [P\textsubscript{i}]\textsuperscript{2}; k\textsubscript{2nd} = 0.46 ± 0.2 M\textsuperscript{-2} s\textsuperscript{-1}, Figure 3.6b. Above [P\textsubscript{i}] = 136 mM, the dependence on [P\textsubscript{i}] becomes zero order.

The binding of phosphate to the ESM was then followed by \textsuperscript{1}H NMR spectroscopy at room temperature and pH = 8.6. Upon mixing 5 mM 3.1(OH)\textsubscript{2}\textsuperscript{2+} with 333 mM KP\textsubscript{i} (I =

![Figure 3.7](a) Stacked plot of aromatic region of \textsuperscript{1}H NMR spectrum of 5 mM 3.1(OH)\textsubscript{2}\textsuperscript{2+} in the presence of 0.333 M KP\textsubscript{i} at pH\textsuperscript{*} = 8.7. The red circles highlight the disappearance of the 4-py protons of [3.1(OH)\textsubscript{2}]\textsuperscript{2+}; the green squares highlight the fast growth of the 2-py signal of [3.1(O\textsubscript{2}PO\textsubscript{2})]\textsuperscript{1+}, and the blue circle highlight the slow growth of the 2-py signal of [3.1(O\textsubscript{2}PO\textsubscript{2})\textsubscript{3.1}]\textsuperscript{5+}. (b) Decrease in intensity of the signals from the 4-py protons of [3.1(OH)\textsubscript{2}]\textsuperscript{2+} (red circles) with fit to a biexponential equation. The lifetimes are 5.6 ± 0.8 h (fast component) and 120 ± 20 h (slow component). (c) Increase in intensity of signals from the 2-py proton of [3.1(O\textsubscript{2}PO\textsubscript{2})]\textsuperscript{1+} (green squares) with fit to a monoexponetial equation with lifetime of 4.9 ± 0.8 h. And increase in intensity of signals from the 2-py proton of [3.1(O\textsubscript{2}PO\textsubscript{2})\textsubscript{3.1}]\textsuperscript{5+} (blue circles) with fit to a monoexponential equation with lifetime of 160 ± 30 h.
1 M), the intensity of the resonances associated with \(3.1(\text{OH})_2^{2+}\) decreased over ~ 25 days, while peaks (many of which were overlapping) associated with two new compounds grew in over this same time period, Figure 3.7a. Monitoring the integrated intensity, which were normalized by setting the total integration of the DPEN methyl protons to 6, revealed biexponential kinetics for the decrease in \(3.1(\text{OH})_2^{2+}\), which could be accounted for by the disparate kinetics of the appearance of the two new complexes, Figure 3.6a and 3.6c. As the 4-pyridyl protons of \([3.1(\text{OH})_2]^{2+}\) complex decreased in intensity, Figure 3.6a and 3.6b red circles, a new set of 4-pyridyl protons grew in, with the same biexponential kinetic behavior, at a new location slightly downfield (7.73 ppm). The kinetic behavior of this growth could be deconvoluted by analyzing the growth of two new set of 2-pyridyl protons. The peak at 8.87 ppm (blue circles in Figure 3.6a and 3.6c) grows in with a lifetime of 4.9 ± 0.8 h, which is the same, within error, of the fast component of the 4-pyridyl decrease (red circles in Figure 3.6a), 5.6 ± 0.8 h. While the peak at 9.34 ppm (green circles in Figure 3.6a and 3.6c), grows in at a much slower rate, with a lifetime of 160 ± 30 h, which is the same within error of the slow component of the 4-pyridyl decrease (red circles in Figure 3.6a), 120 ± 20 h. This data is consistent with the following model:

At \(I = 1\) M and pH = 8.6, 99 % of the phosphate buffer is the monoacidic form, HPO\(_4^{2-}\); therefore, we attribute the faster reaction to the formation of the 1:1 complex, \(3.1(\text{O}_2\text{POOH})^{2+}\), which may be deprotonated at pH = 8.7, Scheme 3.6. This would be consistent with the second order dependence on P, Figure 3.6, since 2 eq. of HPO\(_4^{2-}\) would be required to facilitate acidolysis of the two \(\eta\)-OH ligands required for ligand exchange. In the subsequent slower reaction, deprotonated \(3.1(\text{O}_2\text{POOH})^{2+}\) may react with another

\[
\begin{align*}
3.1(\text{OH})_2^{2+} + 2 \text{HPO}_4^{2-} & \rightleftharpoons K_1 3.1(\text{O}_2\text{POOH})^{1+} + \text{PO}_4^{3-} \\
3.1(\text{O}_2\text{POOH})^{1+} + 3.1(\text{OH})_2^{2+} + 2 \text{HPO}_4^{2-} & \rightleftharpoons K_2 3.1(\text{O}_2\text{PO}_2)3.1^{5+} + 2 \text{PO}_4^{3-}
\end{align*}
\]
\[ \text{3.1(OH)}_2^{2+} \] to give the dimer structure, \[ \text{3.1(O}_2\text{PO}_2)\text{3.1}^{5+} \], which is known to be a stable species in a similar metal-ligand architecture.[10]

Using this model for \( \text{P}_i \) binding, a lower limit for the association constants could be estimated from the relative distributions of the bound and unbound complexes after 25 days. From the NMR integrations, the concentration of the DPEN containing species near equilibrium (after 599 h) was found from their relative ratios; \[ [\text{3.1(OH)}_2^{2+}] = 0.16\times[\text{3.1}]_T = 0.8 \text{ mM}, \]
\[ [\text{3.1(O}_2\text{POO)}]^{1+} = 0.24\times[\text{3.1}]_T = 1.2 \text{ mM}, \]
\[ [\text{3.1(O}_2\text{POO})\text{3.1}^{5+} = 0.6\times([\text{3.1}]_T/2) = 1.5 \text{ mM}. \]

From mass balance considerations, the concentrations of the phosphate species can be calculated to be \( [\text{HPO}_4^{2-}] = 325 \text{ mM} \) and \( [\text{PO}_4^{3-}] = 5.7 \text{ mM} \), and the equilibrium constants are then determined by having reasonable estimates for the concentrations of all relevant species.

We note that this is a preliminary model for the anation of \textbf{3.1} by \( \text{P}_i \); a comprehensive investigation of this reaction, which would be required to fully validate the model, is beyond the scope of the current study. The two relevant association constants were estimated to be \( K_1 = 0.08 \text{ M}^{-1} \) for formation of 1:1 complex and \( K_2 = 0.5 \text{ M}^{-1} \) for the dimer structure. Without more kinetic data collected at room temperature, it is difficult define precisely the rate constants associated with these equilibrium constants because the order in \( \text{P}_i \) was not determined under these experimental conditions. However, the salient feature of this result is that at room temperature, the binding of \( \text{P}_i \) is slow, as compared to \( \text{B}_i \), taking days to reach equilibrium.

To confirm the viability of the proposed 1:1 complex, \[ \text{3.1(O}_2\text{POOH)}^{2+} \], crystals were grown from a mixture of \[ \text{3.1(OH)}_2^{4+} \] and 10 equivalents of \( \text{P}_i \) following a reaction at 90 °C for 3 days at \( \text{pH} = 3 \). The solid-state structure is presented in Figure 3.8, and indicates a 1:1 binding between \textbf{3.1} and \( \text{P}_i \), which is presumably stable with respect to formation of \[ \text{3.1(O}_2\text{PO}_2)\text{3.1}^{5+} \] due to the lower \( \text{pH} \) of the crystallization conditions as compared to the room temperature kinetics measurements. Though a crystal structure of a \( \text{B}_i \) conjugated species could not be obtained, a Job plot was constructed from a titration of \[ \text{3.1(OH)}_2^{2+} \]
with B$_i$ (Figure 3.9), which peaked at a molar fraction of B(OH)$_3 = \sim 0.5$, consistent with a 1:1 binding, in an ostensibly analogous bridging manner as seen in the crystal structure in of 3.1(O$_2$POOH)$_2^+$.

Despite having a binding constants only two orders of magnitude greater than that of P$_i$, the kinetic behavior of B(OH)$_3$ binding to the ESM was dramatically different. To measure the rate constant for B(OH)$_3$ binding at room temperature, it was found that stopped-flow kinetics were required. The extent of the reaction could then be monitored by

**Figure 3.9** Job plot from a titration of [3.1(OH)$_2]^2^+$ with B$_i$ at pH 8.6. The peak is near the 0.5 mole fraction of B(OH)$_3$ (dotted line) which is indicative of 1:1 binding between these species.
following the growth (seen in Figure 3.4a) at λ = 390 nm. Under pseudo first-order conditions, the data was be excellently modeled with a monoexpotential expression, Figure 3.10 (all fits, not shown, possess R² values exceed 99.9 %). The observed rate constant varied linearly with \([\text{B(OH)}_3]\), Figure 3.10b, implying a first order dependence as expected from the Job plot, and from the slope the second order rate constant was found, \(k_{\text{Bi}} = 1.31 \pm 0.04 \times 10^1 \text{ M}^{-1} \text{s}^{-1}\) at 25 °C.

Figure 3.11 Eyring plot of the second order rate constant of the binding reaction of B(OH)₃ to \([3.1(\text{OH})_2]^2⁺\). From the slope, the activation enthalpy was found to be \(\Delta H^\ddagger = 34.5 \pm 0.7 \text{ kJ mol}^{-1}\) and from the y-intercept the activation entropy was found to be \(\Delta S^\ddagger = -107 \pm 3 \text{ J mol}^{-1} \text{ K}^{-1}\).
Variable temperature experiments were also conducted, and an Eyring analysis, Figure 3.11, of the data revealed an activation enthalpy of $\Delta H^\ddagger = 34.5 \pm 0.7$ kJ mol$^{-1}$ and $\Delta S^\ddagger = -107 \pm 3$ J mol$^{-1}$ K$^{-1}$ consistent with a highly ordered transition state that does not involve breaking of an inert Co(III)–O bond, which would lead to a much higher activation enthalpy.$^{13}$ For example, the activation enthalpy for anation reactions of Co(NH$_3$)$_5$(OH)$_2$$^{3+}$ with common anions, such as H$_2$PO$_4^-$, Cl$^-$, and Br$^-$, are all greater than 100 kJ mol$^{-1}$.$^{14}$

### 3.2.3 Influence of [B$_i$] on water oxidation activity of Co-OECs

The current density associated with water oxidation by thin films of Co-OEC was monitored as a function of [B$_i$]. Films were deposited from either borate buffer, CoB$_i$, Figure 3.12a, or phosphate buffer, CoP$_i$, Figure 3.12b onto glassy carbon rotating disc electrodes. The steady state current density associated with water oxidation was monitored as a function of [B$_i$], applied potential, and rotation rate. For both types of films, there exist two regions of interest. At low [B$_i$], the current density depends on the rotation rate, and seems to decrease as the [B$_i$] is lowered. This behavior is indicative of mass transport control of protons away from the films mediated the of buffer from solution to the catalyst.

**Figure 3.12** Dependence of [B$_i$] on the water oxidation current density of 24 mC/cm$^2$ thick films of (a) CoB$_i$ and (b) CoP$_i$ at pH = 8.6 and I = 1 M using a rotating disc electrode at potentials vs. Ag/AgCl of 0.95 V (red), 0.925 V (green), 0.90 V (blue), and 0.875 V (magneta). The shaped data points correspond to rotation rates in rpm of 2500 (square), 1600 (circle), 1225 (up triangle), 900 (down triangle), and 625 (diamond).
film,\textsuperscript{15} which is the reason the transition into this region appears at higher [B\textsubscript{i}] when applying a more positive potential. At higher current densities, production of H\textsuperscript{+} within the films is faster, overwhelming the buffering capacity at higher concentrations.

As [B\textsubscript{i}] is increased further, a second region appears, which is distinguished by a current density that does not depend on rotation rate, indicating activation controlled catalysis.\textsuperscript{16} As highlighted by the linear fits in Figure 3.12, within this region an inverse dependence on [B\textsubscript{i}] is observed. For Co-B\textsubscript{i} films, Figure 3.12a, the slopes reside between –0.52 and –0.42, while CoP\textsubscript{i} films, Figure 3.12b, have slopes that are significant lower, –0.20 and –0.16. Similar experiments on CoB\textsubscript{i} films were also conducted at pH = 9.2, and the slopes in the activation controlled region were in accordance with the data collected at pH = 8.6, Figure 3.13.

![Figure 3.13](image)

**Figure 3.13** Dependence of [B\textsubscript{i}] on the water oxidation current density of 24 mC/cm\textsuperscript{2} thick films of CoB\textsubscript{i} at pH = 9.2 and I = 1 M using a rotating disc electrode at potentials vs. Ag/AgCl of 0.95 V (red), 0.925 V (green), 0.90 V (blue), and 0.875 V (magenta). The shaped data points correspond to rotation rates in rpm of 2500 (square), 1600 (circle), 1225 (up triangle), 900 (down triangle), and 625 (diamond). The slopes of the lines are: –0.52 (red), –0.48 ± 0.3 (green), –0.44 ± 0.3 (blue), and –0.45 ± 0.1 (magenta).

### 3.3 Discussion

The disparate kinetics for the binding of these two common buffer species to [3.1(OH)\textsubscript{2}]\textsuperscript{2+} can be explained by considering the types of bonds that are broken during the
course of the binding event. As the Lewis acidic B(OH)₃ is the binding agent when B₃
buffer is used, the electron density of one η-OH ligand can donate directly into empty p-
orbital of the boron atom forming a tetrahedral borate species. The reaction is likely limited
by a condensation reaction with the adjacent η-OH ligand, yielding a bridging borate
species, as has been proposed for B₃ binding to FeOOH.¹⁷ On the other hand, the Co–OHₓ
bonds that must be broken to form 3.1(O₂POOH)²⁺ are much stronger, since Co(III) is an
inert metal ion with a d⁰ low spin electronic configuration. Since uncoordinated HPO₄²⁻ is
a poor Lewis base, coordination to a Co³⁺ ion must occur to increase its susceptibility to
nucleophilic attack. This anation mechanism is usually rate limited by dissociative
cleavage of the inert Co–OH₂ bond (Co–OH are too strong to be broken).¹⁸

Even though the Co₂(OH)₄ motif did not prove to be active for water oxidation
catalysis within the DPEN framework, if the active edge sites of the Co-OEC possess the
same geometric arrangement, then a model for the interaction of B₃ and P₃ with these edge
sites, Scheme 3.7, can now be proposed in light of the binding studies presented herein. It
is known that the resting state of the Co-OEC catalyst undergoes an oxidative PCET step

**Scheme 3.7 Model of B₃ and P₃ Interaction with edge site of Co-OEC**

![Scheme 3.7 Model of B₃ and P₃ Interaction with edge site of Co-OEC](image-url)

- **Fast Pre-equilibrium**
  - + B(OH)₂, − H₂O
  - + H₂O, − B(OH)₃

- **Active Catalyst**
  - + H₃PO₄, − 2H₂O
  - + 2H₂O, − H₃PO₄

- **Resting State**
  - − H⁺, − e⁻
to form the active species.\textsuperscript{19} If a competitive binding mechanism were operable, an inhibitory effect on water oxidation catalysis may be expected with increased buffer concentration as fewer edge sites would be available to participate in this PCET activation. It is known that at high buffer concentrations there is no dependence of \( [P_i] \) on water oxidation by Co-OEC\textsuperscript{19}. Considering the results above, this observation is not surprising as \( P_i \) binding kinetics are likely too slow to establish a preequilibrium sufficiently fast to influence the electrochemically driven rate of catalysis. However, \( B_i \), in the form of \( B(OH)_3 \), is now shown to bind rapidly to the ESM. Therefore, if the same geometric motif is responsible for catalyst, then an inverse dependence on borate buffer concentration would be expected, as is observed for a similar water oxidation catalyst based on nickel.\textsuperscript{20}

The inverse dependence observed in both films provides validation of the model presented in Scheme 3.7. That the order is not a full first order (which would be indicated by a slope of \(-1\)) may be attributed to either a broad binding isotherm (weakly associated \( B(OH)_3 \)) or a possible parallel mechanism from an active site that does not interact with \( B_i \).\textsuperscript{21} The former possibility may be consistent with the lower slope observed for CoPi films, as active edge sites could be irreversibility capped by phosphate anions during deposition. This would effectively decrease the surface concentration of the \( B(OH)_3 \) binding partner, which could lead to a lower slope as compared to CoB\textsubscript{i} at the same \([B_i]\).

### 3.4 Conclusion

The results presented here highlight the importance of molecular models for understanding the effect buffer species have on Co-OEC. We posit that the nature of \( B_i \) binding to Co-OEC (via \( B(OH)_3 \)) is the same in other amorphous metal oxide water oxidation catalysis. Specifically, we now revise the model for the effect of \( B_i \) on the mechanism of water oxidation by Ni-OEC films. The Tafel data of Ni-OEC was initially interpreted with an inverse third order dependence on \([H^+]\) and inverse first order dependence on \([B(OH)_4]^-\)\textsuperscript{20}. In light of our new understanding of how \( B_i \) binds to the ESM,
we now favor a model involving an inverse second order in \([\text{H}^+]\) (which is coupled to the loss of two electrons) and an inverse first order in \([\text{B(OH)}_3]\). Given that a \(–1\) reaction order in \(\text{B}_1\) is observed for Ni-OEC films, it is likely that the edge sites of Ni-OEC are more Lewis basic than those of Co-OEC. Since the average oxidation state of Ni-OEC in its resting state, +3.7, is greater than that of Co-OEC,\(^{22}\) we suggest that the terminal aqua ligands at the edges of Ni-OEC are more acidic than those of Co-OEC, resulting in a greater concentration of adjacent Ni-OH capable of binding to \(\text{B(OH)}_3\).

Furthermore, our results have implications for the optimization of water splitting devices comprising Co-OEC or Ni-OEC anodes. When using \(\text{B}_1\) buffer as the electrolyte, a balance must be found between the necessity of \(\text{B(OH)}_4^-\) as a proton acceptor, and the inhibitory effect of \(\text{B(OH)}_3\). It would be useful in this context to determine the optimum \([\text{B}_1]\), which would be especially important when running these catalysts at near-neutral pH (\(<9\)).

Finally, these results support the proposal made in Chapter 2 that the inverse dependence on the buffer (\(\text{MeP}_i\)) during film deposition was due to a hydrogen bonding interaction. We have now shown that the rate of inner sphere binding of \(\text{P}_i\) to the molecular ESM is too slow to allow for a mechanism of this type to partake in a preequilibrium fast enough to influence the electrochemically driven rate of deposition. However, the irreversible binding of \(\text{P}_i\) could explain why the domain sizes of as-deposited \(\text{CoP}_i\) are smaller as compared to \(\text{CoB}_i\). Irreversible binding of the \(\text{P}_i\) to the edges of growing \(\text{CoP}_i\) may inhibit film growth, driving deposition to new nucleation sites, as opposed to continued enlargement of established domains. On the other hand, \(\text{B}_i\) species that occupy edge sites of \(\text{CoB}_i\) films may be easily displaced by incoming Lewis acid \(\text{Co(II)}\) ions, thereby allowing for the growth of domains of higher nuclearities. Going forward, these insights will be important for developing strategies to control the domain sizes of electrodeposited Co and Ni-OECs.
3.5 Experimental Methods

3.5.1 Materials

Co(NO$_3$)$_2$·6H$_2$O (Alfa Aesar or Strem), H$_2$O$_2$ 30 % solution in water (Sigma-Aldrich), 2-fluoropyridine (Sigma-Aldrich), 2-ethylpyridine (Sigma-Aldrich), n-butyllithium (Sigma-Aldrich), KPF$_6$ (Alfa Aesar), Ca(ClO$_4$)$_2$ (Sigma-Aldrich) were purchased and used as received. Buffer solutions were made from KH$_2$PO$_4$ or B(OH)$_3$ (Mallinckrodt) using 18 MΩ cm distilled water from a MilliPore purification system and concentrated KOH (Macron) solutions. Syntheses of 2,7-dichloro-1,8-naphthyridine$^{23}$ and 2,7-dicarboxyl naphthyridine methyl ester$^{24}$ were performed according to literature procedures.

3.5.2 General Methods.

Proton nuclear magnetic resonance ($^1$H NMR) spectra were acquired on an Agilent DD2-600 (600 MHz) or Varian Unity/Inova 500 instrument and chemical shifts were referenced to residual protium in the NMR solvent (HDO = δ 4.79), unless otherwise noted. Mass spectroscopic (MS) data were acquired on a Bruker micrO-TOF-QII LCMS ESI-TOF mass spectrometer in the positive ion mode. All mass spectra were externally calibrated with sodium formate. UV-vis spectra were obtained using a Varian Cary 5000 spectrometer with temperatures maintained using a Quantum Northwest TC125 temperature controller. Quartz cuvettes with 1 cm pathlength were used in all experiments, with the exception of the Job plot experiment, which used 4 mm pathlength cell. Crystal structure data were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device at 100 K. Radiation was supplied from a graphite fine focus sealed tube Mo Kα source (0.71073 Å). Crystals were mounted on a glass fibre using Paratone N oil. Data were collected as a series of φ scans. Data were integrated using SAINT$^{25}$ and scaled with a multi-scan absorption correction using SADABS. The structures were solved by intrinsic phasing methods using SHELXS-97 and refined against F$^2$ on all data by full matrix least squares with SHELXL-97.$^{26}$ All non-
hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. Cyclic voltammogram (CV) experiments were recorded at ambient temperature with a CH Instrument 760D potentiostat with a 3 mm diameter glassy carbon working electrodes, BASi Ag/AgCl reference electrode, and a Pt wire counter electrode. The glassy carbon working electrode was cleaned by polishing on felt with 1 µm alumina followed by 0.3 µm alumina, and then sonicated in 18 MΩ cm distilled water, rinsed with acetone and dried with compressed air. Elemental analysis was performed by Midwest Microlabs (Indianapolis, IN).

3.5.3 Benesi-Hildenbrand Method for Measuring Binding Constant of B(OH)$_3$ to ESM.

Individual samples were made from stock solutions of $[3.1(\text{OH}_2)_2]\left[(\text{NO}_3)_4\right]$ (500 µM) and $\text{KB}_i$ (1 M) with KNO$_3$ added to maintain ionic strength at $I = 1$ M. Aliquots from these stock solutions were combined to give final concentration of $3.1(\text{OH})_2$ = 250 µM and $[\text{KB}_i] = 0$ mM, 5 mM, 10 mM, 20 mM, 40 mM, 60 mM, 100 mM, 225 mM, 325 mM, and 405 mM. All samples were maintained at pH = 8.8, and ionic strength $I = 1$ M with KNO$_3$. The same cuvette was used to measure the absorbance spectrum for each sample. The change in absorbance at 400 nm was plotted, Figure 3a inset, as a function of $[\text{B}_i]_T$ using the following equation:

$$\frac{1}{\Delta \text{Abs}} = \frac{1}{b \Delta \epsilon K_{obs} [\text{B}_i]_T} + \frac{1}{b \Delta \epsilon}$$

The association constant with respect to $[\text{B}_i]_T$, $K_{obs}$, was determined from the ratio between the y-intercept and the slope. The association constant with respect to B(OH)$_3$ was then calculated using the following equation:

$$K_B = K_{obs} \left(1 + \frac{K_a}{[\text{H}^+]}\right)$$

Where $K_a = 10^{-8.6}$ M is the acid dissociation constant of boric acid at $I = 1$ M, $[\text{H}^+] = 10^{-8.8}$ M is the concentration of protons in the experiment.

3.5.4 $P_i$ Binding Kinetics at 70 °C
Stock solutions of 500 µM \([\text{3.1(OH)}_2]^{2+}\) (in 1 M KNO₃) and 333 mM KPi (pH = 8.5) were used to make the samples with final concentrations of \([\text{3.1(OH)}_2]^{2+}\) = 250 µM, and [KPi] = 46 mM, 76 mM, 106 mM, 136 mM, and 167 mM. The total volume of each sample was maintained at 4 mL using 1 M KNO₃. The stock solutions were preheated to 70 °C prior to mixing. The changes in absorbance were monitor from 325 – 625 nm, with each spectra taken at time increments such that at least 3 half-lives were collected. The change at \(\lambda = 390\) nm were fit to a monoexponential expression to obtain \(k_{\text{obs}}\). The \(R^2\) values for all fits were > 0.99. The \(k_{\text{obs}}\) values were plotted versus [Pᵢ] and [Pᵢ]², with the later proving to be more linear from 46 mM to 136 mM.

3.5.5 \(P_i\) Binding Kinetics at room temperature.

A 0.924 mL solution of 5 mM \([\text{3.1(OH)}_2]^{2+}\) and 333 mM KPi was followed by \(^1\)H NMR at room temperature (23 ± 1 °C) over 25 days. The pH* = 8.7, which is related to the measured [D⁺] using a pH meter calibrated with [H⁺] solution in H₂O, and equivalent to pH = 8.5 according to the literature equation, \(^{28}\) pH = 0.929pH* + 0.42.

3.5.6 Stopped Flow Kinetics of B(OH)₃ Binding.

Stopped-flow absorbance spectroscopy measurements were performed using an Applied Photophysics DX.17MV instrument equipped with the Pro–Data upgrade. The temperature was maintained to within ± 0.1 °C of the desired temperature with a Lauda RE106 circulating water bath. A solution of \([\text{3.1(OH)}_2]^{2+}\) in 1 M KNO₃ was made slightly basic (pH = 9) by addition of 0.1 M KOH in 1 M KNO₃, and diluted to a final concentration of 500 µM. B₃ buffer sample solutions (pH = 8.8) were diluted from a stock solution of 500 mM with 750 mM KNO₃ (to maintain I = 1 M). The association rates were measured by rapid mixing of equal volumes of \([\text{3.1(OH)}_2]^{2+}\) and B₃ buffer. Each condition was repeated to obtain ~20 traces, which were then averaged and fit to a monoexponential function to obtain \(k_{\text{obs}}\).

3.5.7 Job Plot for B(OH)₃ Binding.
To a solution of $[3.1(OH)_2]^{2+}$ (18.5 mM, 0.75 mL, pH = 8.6) in a 4 mm pathlength quartz cuvette was titrated with 0.1 mL aliquots of a B$_i$ buffer solution (50 mM, pH = 8.6) until the total volume of the sample was 2.25 mL, and $[[3.1(OH)_2]^{2+}] = 6.2$ mM and [B$_i$] = 33.3 mM. The absorbance at $\lambda = 503$ nm was monitored throughout the titration. The corrected absorbance was plotted versus the mole fraction of B(OH)$_3$ in solution to give Figure S6.  

3.5.8 Rotating Disc Electrode Water Oxidation Experiments.

All experiments were conducted using a CH Instruments 760C or 760D bipotentiostat, a BASi Ag/AgCl, and a Pt-mesh counter electrode. Measurements were conducted using a Pine Instruments MSR rotator and a 5 mm diameter Pt-disk rotating electrode (RDE). All film depositions were carried out in three-electrode electrochemical cell with a porous glass frit separating the working and auxiliary compartments. All rotating disc electrode measurements were performed using a flat bottom five neck flask with a porous glass frit to hold the counter electrode. All experiments were performed at room temperature ($23 \pm 1^\circ$C). A series of buffers with varying concentrations of potassium borate (KB$_i$) and potassium nitrate (KNO$_3$) were made from dilutions of stock 2.5M KNO$_3$ and 0.5M KB$_i$ + 750mM KNO$_3$ pH 8.0 while maintaining the same ionic strength of 1M. The pH of each buffer was adjusted to 8.6 or 9.2 using 0.1 M KOH.

CoB$_i$ films were prepared via controlled-potential electrolysis of 0.1 M KB$_i$ pH 9.2 electrolyte solutions containing 0.5 mM of Co$^{2+}$. To minimize precipitation of Co(OH)$_2$ from these solutions 25 mL of 0.2 M KB$_i$ was added to 25 mL of 1 mM Co$^{2+}$ solution. Depositions were carried out on pre-polished 5 mm diameter rotating disk electrode (RDE) with no rotation using controlled-potential electrolysis at 0.72 V without iR compensation and with passage of 4.17 mC. A typical deposition lasted 20 minutes. Following deposition, films were rinsed by dipping briefly in 0.1 M KB$_i$ pH 9.2 solution to remove any adventitious Co$^{2+}$. CoP$_i$ films were similarly prepared but from electrolyte solutions of 0.1
M KP$_1$ pH 7.0 containing 0.5 mM of Co$^{2+}$ with an applied potential of 0.85 V. A typical deposition lasted 40 minutes.

Catalytic films were deposited on RDE as described above. The films were then allowed to rotate at 50 rpm in the electrolyte solution to equilibrate for 10 min at open circuit potential. The solution resistance of the electrolyte was then measured using A.C. Impedance with an applied potential of 0.825V vs Ag/AgCl. Steady state current densities were then acquired at rotation rates of 2500, 1600, 1225, 900, and 625 rpm over the desired potential range of 0.950 V to 0.875 V in 50mV increments with iR compensation.

3.5.9 Synthesis of Dipyridylethane naphthyridine (DPEN).

Two literature methods were combined in the following adaptation. n-Butyllithium (2.5 M in hexanes, 14.0 mL, 35.0 mmol, 4.60 eq.) was added dropwise to a stirring solution of 2-ethylpyridine (4.67 mL, 40.8 mmol, 5.37 eq.) in 100 mL of THF at –78 °C. The resulting deep red solution was stirred at –78 °C for 30 min. The flask was then removed from the cooling bath, and 2-fluoropyridine (1.51 mL, 17.5 mmol, 2.30 eq.) was immediately added dropwise. The mixture stirred for 1 h as it slowly warmed to room temperature, and then was placed in an oil bath to reflux for 1 h under an atmosphere of N$_2$. The flask was then removed from the oil bath and let cool to room temperature, ~ 30 min. Under positive N$_2$ pressure, solid 2,7-dichloro-1,8-naphthyridine (1.51 g, 7.59 mmol, 1.00 eq.) was added to the stirring mixture, and the flask was returned to the oil bath to reflux for 16 h under an atmosphere of N$_2$. After cooling to room temperature, the reaction mixture was quenched with 100 mL of water, concentrated to remove the majority of the THF, and extracted with 3 × 200 mL of CH$_2$Cl$_2$. Organics were combined, dried over MgSO$_4$, filtered, and concentrated. The residual material was recrystallized from 200 mL of hot MeCN to give 2.84 g of DPEN. The filtrate from the first crystallization could be concentrated and redissolved in 100 mL of hot MeCN to yield a second batch (0.39 g) of crystals of DPEN. Total yield of 3.24 g, 6.55 mmol, 86.3 %. Characterization data for this material ($^1$H NMR, ESI-MS) were in accordance with the literature.
3.5.10 Synthesis of \([(\text{DPEN})\text{Co}_2(\text{OH})_2(\text{OH}_2)_2][\text{(NO}_3)_4]\) ([3.1(OH)_2][\text{(NO}_3)_4]]).

Co(NO\text{3})_2 (0.2 M aq. solution, 14.2 mL, 2.84 mmol) was added to a solution of DPEN (701.5 mg, 1.42 mmol) in 5 mL of acetone. After stirring at room temperature for 20 min, H\text{2O}_2 (9.79 M aq. solution, 290 μL, 2.84 mmol) was added, and the reaction mixture was stirred for 16 h at room temperature. The mixture was then concentrated at 60 °C to a volume of 3 mL to which one drop of 10 % HNO\text{3} was added. Then 50 mL of acetone was quickly added, resulting in the precipitation of a pink solid. The solid was collected on 5 μm nylon filter paper and washed with 20 mL 20:1 acetone:water, then 20 mL of acetone. The pink solid was collected and dried in vacuo overnight. Yield, 879 mg, 0.944 mmol, 66.6 %.

\text{1H NMR} \text{(D}_2\text{O}) \ δ 9.20 (d, 4H), \ δ 8.98 (d, 2H), \ δ 8.70 (d, 2H), \ δ 8.35 (m, 8H), \ δ 7.88 (q, 4H), \ δ 3.20 (s, 6H).

\text{HR-ESIMS} \text{ Calculated for } [3.1(\text{OH})_2]^+ - 2(\text{H}_2\text{O}) - 2(\text{H}^+) + (\text{NO}_3^-)]^+: 706.07; \text{ Found } 706.0668.

\text{Elemental Analysis. Theory: C 41.30, H 3.47, N 15.05. Found: C 41.20, H 3.51, N 14.85.}

3.5.11 Preparation of crystals of [3.1(\text{OH})_2][\text{(HO}_2\text{3.1]}][\text{(PF}_6)_6]].

[3.1(OH)_2][(\text{OH}_2)_2][(\text{PF}_6)_6]] (200 mg, 0.215 mmol) was dissolved in 9.5 mL of H\text{2O}. To this solution KPF\text{6} (6 eq., 1.25 mmol, 238 mg in 9 mL of H\text{2O}) was added. The pH of the mixture was raised to 5.5 by the added of ~ 7 drops of 0.5 M KOH, causing the formation of a pink precipitate. The precipitate was collected on 5 μm nylon filter paper and washed with 20 mL diethylether. Crystals suitable for x-ray diffraction were grown from a room temperature aqueous solution of this material at a concentration of 10 mg/mL.

3.5.12 Preparation of crystals of [3.1(\text{O}_2\text{PO(OH))}][(\text{ClO}_4)_2]].

[3.1(OH)_2][(\text{NO}_3)_4]] (43.1 mg, 0.0463 mmol, 1 eq.) and Na_2\text{HPO}_4 (66.0 mg, 0.462 mmol, 10 eq.) were dissolved in 2 mL of H\text{2O}. Three drops (~10 μL) of concentrated H\text{3PO}_4 were then added to make the solution pH = 3. This mixture was heated at 90 °C for 3 days. After this time period, the mixture was cooled to room temperature and Ca(\text{ClO}_4)_2 (1.1 g, 4.63 mmol, 100 eq.) was added. The precipitate was filtered and the filtrate was stored in
a 4 °C refrigerator for 4 days, at which point large red/orange needle-like crystals, suitable for x-ray diffraction, appeared.
3.6 Crystallographic Tables

<table>
<thead>
<tr>
<th>Table 3.1. Crystal data and structure refinement for $[\text{3.1(OH$_2$)$_2$(HO)$_2$3.1}][(\text{PF$_6$})_6]$</th>
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<tr>
<td><strong>Empirical formula</strong></td>
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<td><strong>$\lambda$ (Å)</strong></td>
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<tr>
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</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
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<tr>
<td><strong>GOF$^a$ on $F^2$</strong></td>
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<td><strong>R1$^b$ ($I &gt; 2\sigma$)</strong></td>
</tr>
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<td><strong>R1 (all data)</strong></td>
</tr>
<tr>
<td><strong>wR2 (all data)</strong></td>
</tr>
<tr>
<td><strong>Largest diff. peak, hole</strong></td>
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</tbody>
</table>

$^a$GOF = $(\Sigma w(F_o^2 - F_c^2)^2/(n-p))^{1/2}$ where $n$ is the number of data and $p$ is the number of parameters refined.

$^b$R1 = $\Sigma ||F_o|| - |F_c||/\Sigma |F_o|$. $^c$wR2 = $(\Sigma (w(F_o^2 - F_c^2)^2)/\Sigma (w(F_c^2)^2))^{1/2}$. 
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<td>c (Å)</td>
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<td>V (Å³)</td>
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<td>R1 I &gt; 2σ</td>
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<td>R1 (all data)</td>
<td>R₁ = 0.1089</td>
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<tr>
<td>wR2 (all data)</td>
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<tr>
<td>Largest diff. peak, hole</td>
<td>1.43/-0.81</td>
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a GOF = (Σ w(F_o^2 - F_c^2)^2/(n - p))^{1/2} where n is the number of data and p is the number of parameters refined.
b R1 = Σ|F_o - |F_c||Σ|F_o|,"wR2 = (Σ (w(F_o^2 - F_c^2)^2))/Σ (w(F_o^2)^2))^{1/2}.  

Table 3.2. Crystal data and structure refinement for [3.1(O_2PO(OH))][(ClO_4)_2]
3.7 References


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(27) Anslyn, E. V.; Dougherty, D. A. Modern physical organic chemistry; University Science: Sausalito, CA, 2006, pg. 221.


Chapter 4 — Impurity Based Water Oxidation, Synthetic Modification, and Electron Transfer Properties of Co₄O₄ Cubanes

*Portions of this chapter have been published*


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4.1 Introduction

In Chapter 1 Co₄O₄ cubanes were introduced as molecular models of the Co-OEC. Specifically, Co₄O₄(OAc)₄(Py)₄ (4.1), first synthesized by Das and coworkers,¹ and a related Co₄O₄ cubane of Christou (Co₄O₄(OAc)₂(bpy)₄²⁺)² were used to gain valuable insights into the electronic characteristics and proton-coupled electron transfer (PCET) behavior of a Co(II/IV) couple in a Co-OEC-like ligand environment.³⁴ During the course of our studies detailed in chapters 2 and 3, reports were published that asserted cubane Co₄O₄ clusters, such as 4.1 (Figure 4.1), were also active molecular water oxidation catalysts (WOCs).⁵⁻⁹

The development of soluble molecular WOCs based on Co¹⁰⁻¹³ as well as other transition metals, such as Ir,¹⁴ Ru,¹⁵ Cu,¹⁶ and Fe¹⁷ have also been a subject of intense focus.

![Figure 4.1.](image1.png)

**Figure 4.1.** (left) Line drawing of Co₄O₄ cubanes 4.1 and 4.2. Thermal ellipsoid representation of (middle) 4.1, where the crystallographic data has been taken from ref [1], and (right) 4.1[PF₆] at the 50% probability level. Hydrogen atoms and an acetonitrile molecule have been omitted for clarity. Atoms are color-coded: gray (carbon), blue (nitrogen), red (oxygen), dark blue (cobalt), green (fluorine), and yellow (phosphorous).

Molecular WOCs are attractive research targets because, in principle, they provide a tractable means to characterize catalytic mechanisms and to identify reactive intermediates, thus forming the basis for the continued development of new WOCs. However, the true
identity of the active catalyst must be clarified prior to a detailed interrogation of the WOC mechanism. Indeed, some molecules that were thought to be WOCs have subsequently been shown to be precursors of heterogeneous or colloidal materials, which are the active catalysts.18–21

Proper catalyst identification is especially challenging for the study of molecular cobalt WOCs because extremely small amounts of Co-OEC may be produced from the decomposition of the molecular catalyst.22,23 An exemplar of this challenge is the all-inorganic cobalt polyoxometalate $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_{9}\text{O}_{34})_2]^{10–}$ (Co$_4$POM), which was suggested as a WOC.24 Re-examination of the molecule showed that electrochemically-driven oxygen evolution arose from the formation of Co-OEC on glassy carbon (GC) electrodes at 1.1 V vs. Ag/AgCl.22 Because the Co$_4$POM was unstable at higher potentials, water oxidation activity could not be conclusively attributed to the Co$_4$POM as opposed to its role as a molecular precursor to Co-OEC.25 The Co$_4$POM has now been suggested to exhibit water oxidation activity but under specific photochemical conditions where Ru(bpy)$_3^{3+}$ is the oxidant.26,27 In our previous investigations into the Co$_4$O$_4$ cubanes, we had found no evidence that would be consistent with molecular WO catalysis. Motivated by the recent reports to the contrary and subsequent computational work outlining a detailed mechanistic pathway for 4.1 as a WOC,28 we renewed our investigation of these molecules.

In the bulk of this chapter, we present our results demonstrating that a Co(II) impurity in as-synthesized cubane 4.1 is responsible for the reported catalytic water oxidation activity. We present a series of experiments that are useful for determining whether a small amount of a Co(II) impurity may lead to formation of a heterogeneous WOC. We emphasize the utility of differential electrochemical mass spectrometry (DEMS) for clarifying how anodic potentials affect the decomposition of glassy carbon electrodes, which are commonly used in the study of WOCs. The reported experiments are aimed at
establishing a standardized approach to evaluate the presence of Co(II) impurities in molecular complexes under investigation as water oxidation catalysts.

We also present electrochemical studies of Co₄O₄ cubanes in non-aqueous solvents. We show that in these solvents, the neutral cubanes may be oxidized by two electrons yielding a formal oxidation state of Co(IV)₂Co(III)₂. We also show that these cubanes may be synthetically modified with functionalized carboxylates, which opens new avenues for exploring the photo-induced ET properties of these complexes.

4.2 Impurity Based Water Oxidation

4.2.1 Crude and Purified Co₄O₄ cubanes.

We synthesized and isolated 4.1 by precisely following the one-pot procedure developed by others. Despite satisfactory elemental analyses for multiple batches of as-synthesized 4.1 (Table 4.1), we determined that this material, which was isolated from concentrating a dichloromethane (DCM) extraction, was not pure.

Table 4.1. Elemental Analysis Results for Batches of 4.1

<table>
<thead>
<tr>
<th>Element</th>
<th>Calcd.</th>
<th>4.1 Batch A</th>
<th>4.1 Batch B</th>
<th>4.1 Batch C</th>
<th>4.1 Purified</th>
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<td>C</td>
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<td>N</td>
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<td>6.47</td>
<td>6.45</td>
<td>6.48</td>
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</table>

The presence of impurities was indicated by the observation of many small peaks in the ¹H NMR spectrum (Figures 4.2) and by the presence of slowly moving bands that eluted behind the product band on a silica thin layer chromatography (TLC) plate (Figure 4.2 inset). Based on the TLC result, purification of the compound was performed by
column chromatography on silica. As the complex is uncharged and its metal-ligand bonds inert, elution through silica with a common polar solvent system such as MeOH in DCM allowed for the separation of the desired material without appreciable decomposition. Along with the slowly moving green bands, a red coloration was consistently observed at the top of the column. A comparison of $^1$H NMR spectra for crude (i.e., as-synthesized) and purified 4.1 is shown in Figure 4.2. Several peaks that are observed in the aromatic region in the NMR of the crude sample are absent in the NMR of the purified sample. Molecular impurities are also indicated by many peaks in the m/z range of 300–700 in the ESI-MS of crude 4.1; these peaks are absent in the purified sample (Figure 4.3).

Figure 4.2. A comparison of the $^1$H NMR spectra of (black line, —) 10 mM crude 4.1 and (red line, —) 10 mM pure 4.1 in D$_2$O. Upper right inset, a comparison of TLC for left, crude 4.1, and right, purified 4.1, on silica with 5% methanol in dichloromethane mobile phase.

A structural variant, 4.2, was also synthesized according to Das’ original procedure; the final product was isolated by precipitation and filtration. No diamagnetic impurities were detected in the $^1$H NMR spectra of the precipitated 4.2. However, to remove possible paramagnetic impurities, the precipitated 4.2 was subject to further
purification by chromatography. Interestingly, the same $^1$H NMR spectrum was obtained for precipitated and chromatographed 4.2 (Figure 4.4), though the former was observed to have impurities that were not removed by precipitation. As we shall see in the following sections, this does not mean the complex is free of impurities.

The solid state structure of neutral 4.1 was reported previously, and is reproduced in Figure 4.1. The crystal structure of the oxidized cubane 4.1$^+$ was known as a perchlorate salt. We developed a reliable chemical oxidation of 4.1 using Ce(IV) as an oxidant in MeCN. The oxidized cubane 4.1$^+$ could then be isolated as a PF$_6^-$ salt, as shown in Figure 4.1 (right).
4.2.2 Electrochemical Water Oxidation

The reported water oxidation activity of 4.1 could not be replicated using purified samples. Figure 4.5 compares the CVs of crude and purified 4.1 (0.852 mg/mL, 1 mM assuming 100% purity). The catalytic current, peaking at 1.3 V (all potentials are

Figure 4.4 ¹H NMR spectrum of 10 mM (left) purified 4.2 and (right) crude 4.2 in D₂O. Inset: magnification of the aromatic region of the spectrum.

Figure 4.5 Background corrected CVs of crude (–, black) and purified (–, red) samples of 4.1 (0.852 mg/mL) in 0.2 M KPi buffer, pH = 7. Two scans are presented for the crude sample demonstrating the loss of activity upon the 2nd scan. Crossed arrow indicates initial point and direction of scan.
referenced to Ag/AgCl), in the crude sample is consistent with the WOC activity that has been previously reported of 4.1 in the presence of proton accepting electrolytes. However, a similar catalytic wave in the purified sample is completely absent; only a reversible Co(III)$_3$Co(IV)/Co(III)$_4$ couple centered at $E_{1/2} = +1.05$ V is observed. Interestingly, the catalytic current detected with the crude sample is only prominent in the first scan of the CV.

A similar behavior is observed for 4.2 where precipitated samples exhibit a large catalytic current in the CV whereas a chromatographed samples show only the reversible Co(III)$_3$Co(IV)/Co(III)$_4$ couple, as shown in Figure 4.6a and 4.6b. The $E_{1/2}$ of the

![Figure 4.6](image)

**Figure 4.6** (a) CVs showing two full scans of (red line, —) 2 mM crude 4.2 and (black line, —) no analyte in 0.2 M KP$_1$ (pH = 7). (b) CVs showing two full scans of (red line, —) 2 mM pure 4.2 and (black line, —) no analyte in 0.2 M KP$_1$ (pH = 7). The arrows and crosses indicate the initial point and direction of scans. (c) CVs (red line, —) comparing crude 4.1 (0.852 mg/mL) and (d) purified 4.1 (0.852 mg/mL) in 0.2 M carbonate buffer. The background CVs (black line, —) are provided for comparison.
A reversible couple is at a more positive potential than for 4.1 due to the electron withdrawing nature of the methyl ester substituents on the pyridine ligands.

The electrochemistry of 4.1 was also investigated in carbonate buffer at pH = 7. The crude sample also showed a catalytic current that peaks at a potential slightly less positive than 1.4 V (Figure 4.6c and 4.6d), which was absent in the purified sample. The only observed difference between the CVs in carbonate and phosphate electrolyte is that the catalytic peak current of the crude sample occurs at a more positive (ca. 80 mV) potential in carbonate electrolyte.

To confirm that the catalytic current in the crude sample was associated with the oxygen evolution reaction, electrochemical oxidation was performed in a DEMS experimental setup, which allows for the immediate and simultaneous detection of all

![Figure 4.7 DEMS experimental data for three samples: (a) crude 4.2, (b) purified 4.1 and (c) purified 4.2. Top panels are the Faradaic current density; middle and bottom panels are mass channel 32 (O2) and mass channel 44 (CO2) m/z, respectively. Red lines are representative data from the samples, and black lines are the data from the corresponding blank GC electrodes.](image-url)
gaseous products formed at the electrode surface.\textsuperscript{30} The catalytic current from an unpurified sample shown in the red trace of the top of Figure 4.7a is accompanied by the production of O\textsubscript{2}, as shown in the middle panel of Figure 4.7a. Purified \textbf{4.1} and \textbf{4.2} were also investigated using DEMS under the identical conditions employed for that of the crude sample. As shown in the top panels of Figures 4.7b and 4.7c for purified \textbf{4.1} and \textbf{4.2}, respectively, the Faradaic current density decreases by over an order of magnitude from that of the crude sample. The waveform of the CVs in Figure 4.7 are different than those in CVs on stationary GC electrodes (e.g. Figure 4.5, red trace) owing to the flowing of the electrolyte in the DEMS experiment; similar waveforms are observed for instance at rotating disk electrodes where there is forced solution flow across an electrode surface.\textsuperscript{31} The signal from the mass channel of O\textsubscript{2} for the purified samples (middle panels in Figures 4.7b and 4.7c) shows no O\textsubscript{2} production for applied potentials below 1.4 V; at potentials of 1.4 V or greater, an extremely small amount of O\textsubscript{2} is observed (pA intensities as opposed to the nA magnitudes of crude samples). We note that in all three samples, the mass channel of CO\textsubscript{2} exhibits a sizable signal when the electrode potential surpasses ~1.2 V. The high level of evolved CO\textsubscript{2} is observed even in the background scans of blank GC electrodes (black lines in the bottom panels in Figures 4.7a–c).

We sought to place a limit on the level of O\textsubscript{2} produced by the cubane cluster within the error of our measurements. The middle panel of Figure 4.7b indicates that there is a small but non-negligible amount of O\textsubscript{2} produced in purified samples of \textbf{4.1} at applied potentials >1.4 V. We therefore wished to quantify the amount charge passed with the current associated with the slight downturn in the red CV trace at potentials above 1.4 V in Figure 4.5. Three separate voltammograms (using three independently prepared GC electrodes) were collected with a sample of purified \textbf{4.1} (black traces in Figures 4.8b–d). A simulated CV (Figure 4.8a) was subtracted from the background corrected raw data to remove the current that is due to the reversible Co(III)\textsubscript{3}Co(IV)/Co(III)\textsubscript{4} couple, thus leaving
only the current that may be attributed to oxygen evolution (red traces in Figures 4.7b–d).

From these data, the average current density was $0.11 \pm 0.04$ mA/cm$^2$ at 1.5 V. By making the conservative assumption that all of this current leads to the production of $O_2$, then a TOF of 0.06 mol $O_2$/mol catalyst is calculated at an overpotential of 0.89 V (see section 4.5.18 for details). This low current density and TOF is consistent with catalysis from ppb Co(II) produced from decomposition of the cubane (see section 4.5.18).

To exclude the possibility of chemistry specific to a 4.1:GC interaction, Pt, Au, and FTO were also employed as electrode materials. In all three cases, a similar behavior was obtained as for the GC experiments: the CVs of the crude 4.1 showed significant water oxidation current, which was absent in the CVs of the purified material (Figure 4.9).
In addition to electrochemical WOC activity, photochemical water oxidation has been reported for as-synthesized samples of 4.1 using the Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ sacrificial oxidant system. This photochemical method for the in situ production of Ru(bpy)$_3^{3+}$ avoids...
drawbacks associated with using Ru(bpy)$_3^{3+}$ directly as a primary oxidant for water oxidation.\textsuperscript{32} However, as will be discussed in section 4.2.6, caution must be employed when using this method, due primarily to consequences associated with the in situ formation of the highly oxidizing species SO$_4^{2-}$\textsuperscript{•}. The photochemical assay was performed in triplicate according to the literature procedure,\textsuperscript{5} with the exception that phosphate buffer was used instead of carbonate. The solution [O$_2$] were measured for samples of crude 4.1, purified 4.1, and without added catalyst. A fluorescence-based O$_2$ sensor was immersed into N$_2$ purged solutions containing [Ru(bpy)$_3^{2+}$] = 0.5 mM, [S$_2$O$_8^{2-}$] = 35 mM, and [4.1] = 0.33 mM, and the cuvettes were photolyzed with a Hg/Xe arc lamp ($\lambda_{exc} > 400$ nm). The yield of O$_2$ over 400 s of photolysis decreased from 167 ± 15 µM for the crude samples to 31 ± 6 µM for the purified samples (Figure 4.10).

**Figure 4.10** Solution [O$_2$] measurements during illumination of crude samples of 4.1 (●, black), purified 4.1 (—, red), and without added 4.1 (●, green). Photochemical reactions were performed in the presence of 0.5 mM Ru(bpy)$_3^{2+}$, 35 mM Na$_2$S$_2$O$_8$, and 100 mM KPi pH = 7 buffer. The concentration of crude and purified 4.1 was 0.33 mM, assuming 100 % purity for the crude material.
4.2.4 Identification and Quantification of Impurities

To identify and quantify the impurity found in the crude samples of 4.1, a series of spectroscopic and electrochemical experiments were performed. The EPR spectrum of a solid sample of the crude 4.1 reveals a broad paramagnetic signal over the range $g = 10$ to 2, which is absent in the purified sample (Figure 4.11). This signal is consistent with a paramagnetic Co(II) species. To confirm the presence of a Co(II) impurity, EDTA was titrated into a CV solution of the crude sample. Figure 4.12a shows the CVs for the addition of EDTA (0–0.5 mM) into a 2 mM solution (assuming 100% purity) of crude 4.1 in 0.2 M KP$_3$, pH = 7. Nearly complete suppression of the catalytic current was observed at 0.5 mM EDTA addition. As a control, a 50 µM solution of purified 4.1 was treated with 10 mM

![Figure 4.11 EPR spectra of solid samples of (blue line, —) crude 4.1 (Batch A), (red line, —) crude 4.1 (Batch C), and (black line, —) purified 4.1 with 2 mW microwave power and at 70 K.](image-url)
EDTA in 0.2 M KP\textsubscript{i} at pH = 7 for 1 h, and no changes in absorbance were observed (Figure 4.12b), confirming that \textbf{4.1} is kinetically stable in the presence of EDTA. The CV wave of the Co(III)/Co(IV) couple of purified \textbf{4.1} with addition of EDTA (Figure 4.12c) is fully reversible, indicating that \textbf{4.1}+ is also stable to EDTA on the timescale of the CV experiment.

The amount of Co(II) introduced by dissolving the crude preparation of \textbf{4.1} in aqueous media could be quantified by applying \textsuperscript{31}P NMR line broadening analysis, which we previously employed to quantify the self-healing properties of Co-OEC. A calibration
The calibration curve was constructed by adding increasing amounts of a 1:1 mixture of Co(OAc)$_2$:pyridine to a 0.5 mM solution (0.426 mg/mL) of purified 4.1 in 0.2 M KPi buffer (Figure 4.13). This calibration curve was used to determine the amount of Co(II) in batches of crude 4.1. Although CV experiments were performed with 4.1 at a concentration of 0.852 mg/mL, at this concentration of crude 4.1 the broadening of the phosphate signal is too great to construct a calibration curve over a wide enough range. This was due to the presence of a high concentration of paramagnetic species. Thus, we performed $^{31}$P NMR line broadening experiments at half the concentration used for CV experiments. Figure 4.10 shows the $^{31}$P NMR signals of phosphate upon dissolving 0.426 mg/mL of crude 4.1 for three separately prepared batches. Per the calibration curve, we determine that the Co(II) ion concentration in solution is $[\text{Co(II)}] = 0.086 \pm 0.004 \text{ mM}$, $0.091 \pm 0.008 \text{ mM}$, and $0.065 \pm 0.006 \text{ mM}$ for samples (c), (d), and (e), respectively.
and 0.065 ± 0.006 mM for samples (c), (d), and (e), respectively ([Co(II)]\text{avg} = 0.08 ± 0.01 mM). Translating this result to the concentrations used for CV experiments, a sample of 0.852 mg/mL of crude 4.1 introduces an average concentration of [Co(II)] = 0.16 ± 0.02 mM into solution.

The results of the $^{31}$P NMR experiments were confirmed by an electrochemical titration, in which [Co(II)] was correlated with the catalytic current observed by CV (Figure 4.14). With increasing [Co(II)], the peak current of the catalytic wave at 1.3 V increases linearly. A calibration curve was again constructed and used to assess [Co(II)] in the three
batches of crude 4.1 at the concentration used for CV experiments. The results of this assay shows excellent agreement with the $^{31}$P NMR experiment, albeit with larger error bars, giving $0.153 \pm 0.019$ mM, $0.178 \pm 0.020$ mM, and $0.120 \pm 0.016$ mM for the three samples, with a $[\text{Co(II)}]_{\text{avg}} = 0.15 \pm 0.03$ mM.

4.2.5 Characterization of Electrode Surface.

Since crude 4.1 introduces Co(II) into the solution, we would expect that at anodic potentials, Co-OEC will be deposited. Indeed, bulk electrolysis of a 1 mM solution of crude 4.1 at 1.2 V for 5 min resulted in the deposition of Co-OEC material on the electrode surface, which was readily observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (Figures 4.15 and 4.16, respectively). Bulk electrolysis of the crude sample at a higher potential of 1.4 V results in significantly less Co-OEC detected on the electrode surface (Figures 4.15c and 4.16c), despite more charge.

![Figure 4.15 SEM images of GC electrodes after a 300 s bulk electrolysis of (a) crude 4.1 at 1.2 V, (b) purified 4.1 at 1.2 V, (c) crude 4.1 at 1.4 V, and (d) no analyte.](image)
being passed. Per the DEMS experiment, current is redirected from water splitting ($O_2$ production) to degradation of the GC electrode ($CO_2$ production at higher potential).

Although bulk electrolysis performed over 300 s of a purified sample at 1.2 V resulted in an EDS spectrum that is indistinguishable from that of a blank sample (Figure 4.16b and 4.16d), the SEM images of the pure and blank samples showed a subtle difference. The density of light contrast material was increased in the pure sample as compared to that of the blank sample. We therefore pursued further characterization of the electrode surface by XPS analysis, which is more selective to analysis of surface materials than EDS. A comparison of high-resolution Co 2p XPS spectra of crude, pure, and blank GC electrodes after 300 s of bulk electrolysis at 1.2 V is shown in Figure 4.17. A trace signal at the Co 2p$_{3/2}$ peak of the pure sample is barely distinguishable over background.
whereas a large Co 2p3/2 signal is observed for electrodes removed from bulk-electrolyzed solutions of crude 4.1.

### 4.2.6 Discussion of Water Oxidation Catalysis by Co4O4 Cubanes

As-synthesized samples of 4.1 contain significant amounts of impurities in two forms. The many aromatic peaks in the 1H NMR spectra of crude 4.1 (Figure 4.2) and the slowly eluting bands on TLC plates are likely Co(III) clusters of smaller nuclearity, which are known to be stable compounds. Of greater significance, as demonstrated by EPR spectroscopy (Figure 4.11), electrochemical measurements in the presence of the ion scavenging EDTA (Figure 4.12a) and 31P NMR line broadening analysis (Figure 4.13), a Co(II) impurity is present in crude samples of 4.1. Electrochemical titration experiments and 31P NMR line broadening experiments quantify significant amounts of Co(II) in as-synthesized preparations of 4.1. Repeated experiments on different batches of as-synthesized 4.1 show that the concentration of Co(II) is 16% of the expected concentration of the cubane molecule, 4.1. Because the Co(II) impurity is soluble in DCM, the ligation
of the Co$^{2+}$ ion likely involves solubilizing organic groups, such as the acetate or pyridine reactants of 4.1, as salts of Co(II) with outer-sphere anions such as acetate or nitrate are unlikely to have significant solubility in DCM. Ligation of the solubilizing groups appears to be sufficiently weak that Co-OEC is easily formed (vide infra). As a cautionary note, the absence of line broadening in the $^1$H NMR spectra of 4.1 does not provide sufficient evidence that Co(II) is not present in solution. The lack of significant line broadening in the $^1$H NMR spectra upon titrating 1:1 Co(OAc)$_2$:pyridine into a sample of purified 4.1 (Figure 4.18) indicates that this is not a sensitive measure of paramagnetic impurities, presumably because 4.1 (a neutral, weakly basic molecule) does not interact significantly with the Co$^{2+}$ ion. As Figure 4.13 demonstrates, the phosphate $^{31}$P NMR signal is a much more sensitive measure of the presence of Co(II) impurities. The Co(II) ion impurities do not elute on silica and thus are easily removed from 4.1. The same behavior is observed for
where silica gel chromatography can be used to remove Co(II) impurities from as-
synthesized or precipitated samples.

The Co(II) impurity acts as a source for the formation of the known water oxidation
catalyst, Co-OEC. The formation of heterogeneous Co-OEC occurs from solutions of
Co(II) with any proton accepting electrolyte, as long as the concentration of the electrolyte
is sufficiently high to control pH.\textsuperscript{34,35} Moreover, Co-OEC will be formed from Co(II) either
electrochemically or (photo)chemically as long as the potential is sufficient to oxidize Co\textsuperscript{2+}
to Co\textsuperscript{3+} in the presence of electrolytes such as phosphate or carbonate. Consistent with the
formation of Co-OEC, the catalytic wave in Figure 4.5 has the same peak potential and
onset current as found for a CV of Co\textsuperscript{2+} solutions from which Co-OEC electrodeposits
(Figure 4.19). However, unlike a well-behaved catalytic process, as is typical of Co-OEC

![Graph showing CV comparison](image.png)

**Figure 4.19** Comparison of CV using a GC electrode of a 0.852 mg/mL sample of crude
4.1 (---, red line) to a CV obtained from a solution of 150 µM Co(NO\textsubscript{3})\textsubscript{2} in 0.2 M KP\textsubscript{i}
pH = 7 buffer (---, black line). The pre-feature to the catalytic current of solutions of 4.1
is the Co(III)\textsubscript{3}Co(IV)/Co(III)\textsubscript{4} reversible couple of the cubane.
of FTO, a peak response is observed in the cyclic voltammogram. A peak in the catalytic wave will result from either depletion of substrate or catalyst deactivation.\textsuperscript{36} Since the solvent, H\textsubscript{2}O, is the substrate, pH is maintained by a high concentration of phosphate, and current densities are low, we can safely rule out substrate depletion as the cause for the peak in Figure 4.5. A peak will result, however, if the catalyst were to be removed from the electrode in a parasitic side reaction, or as in this case, if oxidative degradation of the electrode is significant (vide infra).

Once the impurities are removed, the large catalytic wave in CVs of solutions of unpurified 4.1 (Figure 4.5) and 4.2 (Figure 4.6b) disappear. This behavior is observed on other electrode materials (Pt, Au, and FTO, Figure 4.9) as well; crude 4.1 shows higher currents at anodic potentials than purified 4.1, providing further evidence that an impurity is responsible for the WOC, as opposed to spurious activity arising from a specific deleterious interaction between the cobalt cubane molecule, 4.1, and a GC electrode. SEM, EDS, and XPS support the formation of a heterogeneous Co catalyst, which we attribute to heterogeneous Co-OEC, on electrodes from bulk electrolyzed solutions of crude 4.1. Even in purified samples of 4.1, XPS indicates that indeed a small amount of cobalt can be detected on the electrode. The production of Co-OEC from purified 4.1 explains the small amount of O\textsubscript{2} observed in the DEMS experiment (Figure 4.7b, middle panel) and the minute amount of current beyond background (Figure 4.5, red trace) at potentials above 1.4 V vs. Ag/AgCl. If all the current at 1.5 V goes to the production of O\textsubscript{2}, the TOF at this potential would be 0.06 mol O\textsubscript{2}/mol 4.1. However, only an extremely small amount of cobalt in the form of Co-OEC is needed to support the current density associated with this TOF. Using the Tafel slope and known dependence of the exchange current density on the thickness (i.e. cobalt content) of films of Co-OEC,\textsuperscript{37} it was determined that only ~70 ppb of 4.1, with its 4 cobalt atoms, would need to decompose to furnish the necessary amount of cobalt in the form of Co-OEC to produce this observed current density (see section
4.5.18 for details of this calculation). We note that the amount of Co-OEC and O\(_2\) produced, however, is negligible as compared to the Co-OEC formed from crude samples of \textbf{4.1}.

At potentials above 1.4 V, the DEMS results show that the observed current is predominantly due to the production of CO\(_2\) when a GC electrode is used as the anode. As EDS and XPS results show, the process is so efficient at 1.4 V, that the current is largely redirected from Co-OEC production from the Co(II) impurity to oxidative degradation of the electrode. Importantly, the direct evidence of CO\(_2\) formation (Figure 4.7a, bottom) under conditions that thermodynamically favor the formation of Co-OEC argues against the possibility that the Co-OEC catalyst is unstable at these high potentials. If the potential is such that the rate of degradation of the GC surface is rapid, as Stracke et. al. have noted\textsuperscript{25} one cannot interpret the absence of deposited heterogeneous material after electrolysis as evidence of actual molecular catalysis, since surface catalyst will be lost upon degradation of the underlying electrode. Consistent with this argument, SEM and EDS analysis show a decrease of observable Co-OEC on the electrode for bulk electrolysis experiments performed at 1.4 V vs. 1.2 V (Figures 4.15 and 4.16). Any carbon material (e.g., graphene, carbon nanotubes, etc.) may be compromised due to degradation at high anodic potentials and thus water oxidation experiments performed on carbon-based anodes should be subject to DEMS or other mass spectrometric analysis to ensure that the current is not due to electrode oxidation to CO\(_2\).

As in electrochemical experiments, removing the Co(II) impurity from photochemically driven WOC also leads to a dramatic reduction in the amount of O\(_2\) observed (Figure 4.10). In the photolysis experiment, persulfate (S\(_2\)O\(_8^{2-}\)) is used as a sacrificial oxidant to form Ru(bpy)\(_3^{3+}\) upon irradiation. The reduction potential of Ru(bpy)\(_3^{3+}\) is 1.06 V vs. Ag/AgCl. At pH = 7, Co-OEC is formed from Co(II) at potentials in the range of 0.75–0.80 V vs. Ag/AgCl\textsuperscript{34} Therefore, under the conditions of the photolysis experiment, Co(II) can be oxidized to Co-OEC by Ru(bpy)\(_3^{3+}\). Furthermore, the
onset of WOC by Co-OEC is 0.90–0.95 V vs. Ag/AgCl, and so Ru(bpy)$_3^{3+}$ is thermodynamically capable of driving catalyst turnover. In addition, the quenching reaction of Ru(bpy)$_3^{2+}$ by persulfate to produce Ru(bpy)$_3^{3+}$, also produces SO$_4^{2-}$ as a potential oxidant, which has ample overpotential to drive water oxidation (E$^\circ$ ~ 2.2 V vs. Ag/AgCl). Thus, the major pathway giving rise to water photooxidation activity with as-synthesized 4.1 is consistent with the formation of Co-OEC from the in situ oxidation of Co(II) ions.

Although all previously published photochemical studies have used as-synthesized 4.1 and thus water oxidation likely originates from Co-OEC, the present study shows the photochemical oxidation of purified 4.1 also results in the production of measurable quantities of O$_2$ (31 ± 6 µM) over 400 s of the photolysis, leading to a TOF = $2.3 \times 10^{-4}$ sec$^{-1}$. At the reduction potential of Ru(bpy)$_3^{3+}$, which within the Co(III)$_2$Co(IV)/Co(III)$_4$ wave (Figure 4.5), no O$_2$ is produced as measured by DEMS (Figure 4.7b). Therefore, Ru(bpy)$_3^{3+}$ is not a potent enough oxidant to turnover 4.1; a greater overpotential is required, if 4.1 is indeed a molecular catalyst under these specific photochemical conditions. As noted above, the protocol of the photochemical experiment produces the strongly oxidizing species SO$_4^{2-}$. This species is free not only to react directly with Ru(bpy)$_3^{2+}$ but also to react with 4.1 because the concentrations of [Ru(bpy)$_3^{2+}$] = 0.5 mM and [4.1] = 0.33 mM are similar. Therefore, the observed O$_2$ emanating from the photolysis conditions used for purified 4.1 in Figure 4.10 is likely due to the interaction of 4.1 with SO$_4^{2-}$, which has a considerably more positive reduction potential than Ru(bpy)$_3^{3+}$.

We envision WOC activity to arise from either oxidation levels beyond a Co(III)$_2$Co(IV) cubane or decomposition of the cubane promoted by SO$_4^{2-}$. Computational investigations into the mechanism of WOC by 4.1 suggest that two oxidations of 4.1 to the level of Co(III)$_2$Co(IV)$_2$ and an acetate ligand dissociation were required prior to water attack and subsequent O–O bond formation. We cannot confirm if SO$_4^{2-}$ is capable of
oxidizing 4.1⁺ because in aqueous solution the electrochemical window available for exploring the higher oxidation states of the cubane is limited; however, as demonstrated in section 4.3.1, the cubanes like 4.1 are reversibly oxidized to Co(III)₂Co(IV)₂ in nonaqueous solvents at potentials ~ 1.1 V more positive than the reduction potential of the Co(III)₃Co(IV) cubane. Therefore, it may be possible for SO₄⁻ to mediate water oxidation by producing a highly oxidized cubane, though turnover via this mechanism would require such extremely high overpotentials that the utility of such a catalytic system must be questioned. Alternatively, SO₄⁻ is capable of breaking the O–H bond (BDFE = 123 kcal/mol)³⁹ of water directly to produce the radical, •OH.⁴⁰ We do not expect the C–H bonds of the ligands, and thus the molecule itself, to be thermodynamically stable with respect to hydrogen atom abstraction given the extreme potentials provided by the electron accepting SO₄⁻ and proton accepting phosphate buffer species. In fact, it is known that acetate (a coordination ligand of 4.1) is oxidized by SO₄⁻,⁴¹ making acetate buffer incompatible with the Ru(bpy)₃²⁺/persulfate photochemical assay. If the cubane were to decompose by the action of SO₄⁻, Co-OEC is a likely product of the decomposition.

It may be useful now to consider the precise nature of the Co(II) impurity. Since the impurity is soluble in DCM, the ligation of the Co²⁺ ion likely involves solubilizing organic groups, acetate and pyridine. However, it is clear that the ligation is sufficiently weak that upon dissolution in water the speciation of the Co²⁺ ion is predominantly that of unligated Co(H₂O)₆²⁺. This is evident from the catalytic wave in Figure 4.5, which has the same peak potential and onset current as found for Co-OEC originating from Co(NO₃)₂ (Figure 4.19). Relatedly, Berlinguette and coworkers reported that the catalytic response in CVs of their purported molecular WOC catalyst, [Co(Py5OMe)(OH₂)]²⁺, was qualitatively similar to that of very low concentrations of unligated Co(H₂O)₆²⁺.⁴² A series of experiments to determine the source of their catalytic current were then performed by these authors, who concluded that the water oxidation was molecular in origin, or at least
not exclusively emanating from the in situ formation of Co-OEC particles on the electrode surface. We will now use CV simulations as a foundation to critically evaluate the efficacy of these and other experiments reported in the literature for identifying true molecular water oxidation catalysis.

Simulation can be used to predict the electrochemical behavior of kinetically labile Co(II) contained complexes. Simulated CVs for a simplified model of Co-OEC catalysis is shown in Figure 4.20 and demonstrates that when the Co(II) source comes from a ligated molecular species, Co(II)L, the magnitude of the binding constant of the ligand, $K_b$, can significantly affect the potential at which catalytic currents are observed. The model was constructed by making the assumption that deposition of Co-OEC (labeled Cat in Figure 4.20) is a fast, irreversible step (step 3) that follows the oxidation of Co(II) to Co(III). A positive shift in the nominal onset potential for catalysis is observed as the binding

![Figure 4.20](image-url)

**Figure 4.20** Simulated CVs for a simplified Co-OEC mechanism beginning from a molecule species, Co(II)L, with log ($K_B$) = 5 (green, -), 10 (blue, --), 12 (pink, -•), 15 (red, - ), and 20 (black, - - ). Right, five step mechanistic sequence used in the simulation.
constant, $K_B$, increases. This effect results from an electrochemical CE mechanism (steps 1 and 2 in the mechanistic scheme of Figure 4.20), which precedes catalyst formation and turnover. It should be highlighted that, despite the observed change in the onset potential of the catalytic current, the nature of the catalytic species in Figure 4.20 does not change. Therefore, we discourage the interpretation of a positive shift in the onset potential relative to that observed for $\text{Co(H}_2\text{O)}_6^{2+}$ as evidence for true molecular catalysis, as is sometimes presented in the literature.\[25\]

Finally, we emphasize that these simulations are built on two fundamental principles of cobalt chemistry: 1) that the high-spin electronic structure of Co(II) species results in fast ligand exchange and conversely, 2) that the low-spin electronic structure of Co(III) species results in slow ligand exchange.\[43\] Therefore, as $\text{Co(II)}_{\text{free}}$ is oxidized to Co(III), irreversible chemical transformations, like condensation and thus Co(III)–O bond-formation, results in the appearance of Co-OEC. This causes the depletion of $\text{Co(II)}_{\text{free}}$ from the solution proximal to the oxidizing species (i.e. the electrode, $\text{Ru(bpy)}_3^{3+}$, or some other chemical oxidant). To satisfy the requirements of the rapid equilibrium, $\text{Co(II)}_{\text{free}}$ is then replenished by further decomposition of the Co(L) species. In other words, Co(L) can act as a cobalt reservoir, effectively buffering $[\text{Co(II)}_{\text{free}}]$ in solution. These considerations lead to the important cautionary note, which has been mentioned by others\[27\] that when studying Co(II)-based molecular WOC, one should not use $[\text{Co(II)}_{\text{free}}]$ that is detected prior to the application of an oxidizing potential as a measurement for the maximum amount of Co(II) available to form Co-OEC. This amount should only be considered as a lower limit, since Co(II) oxidation effectively induces decomposition of the Co(L) species, providing more available Co(II)$_{free}$ as the experiment progresses in time.

As an example, in the case of $[\text{Co(PySOMe)(OH}_2)]^{2+}$, the stability of the complex at pH 7 and 10.98 was established by observing changes in the UV-vis spectrum with time.\[42\] However, this experiment does not address the stability of the complex under anodic
potentials, which is the critical issue. Past the Co(III)/Co(II) reduction potential, the complex will be oxidized to the inert \([\text{Co(Py5OMe)(OH}_2\text{)}]^3+\). This redox transformation is proton coupled and has been characterized in detail.\(^{14}\) Since oxidation of this Co(III) complex is believed to yield the key catalytic species for water oxidation, it is this Co(III) complex that should have been isolated and interrogated as an electrocatalyst. As a d\(^6\), substitution inert, and diamagnetic, this Co(III) complex could have been subjected to all of the tests described earlier in this chapter. Rather the Co(II) complex was interrogated electrochemically, and therefore, the oxidative leaching of Co(II) from the reservoir provided by \([\text{Co(Py5OMe)(OH}_2\text{)}]^2+\) in the bulk solution must be considered as a possible pathway of decomposition, as indicated in the CV simulations above.

We recommend that when studying cobalt-based WOCs that may be isolated as either a Co(II) or Co(III) species, it is preferable to initiate detailed electrochemical and stability studies with the Co(III) species, since this allows for a larger number of definitive tests to be performed. On the other hand, when the potential WOC can only be isolated as a Co(II) species, the \(^{31}\)P line broadening and EDTA titration experiments lose their utility, and distinguishing true molecular catalysis from catalysis due to decomposition to Co-OEC becomes a much greater challenge. This is no better exemplified than in the case of Hill’s Co\(_4\)POM, for which multiple published studies have come to diametrically different conclusions.\(^{22,24,27}\) As a result, the only common ground found by the various authors of these studies is that whether the catalysis is homogeneous or heterogeneous may depend on the specific conditions of the experiment (e.g. oxidant, pH, buffer species, and buffer concentration).

### 4.3 Synthetic Modification and Electron Transfer Properties of Co\(_4\)O\(_4\) Cubanes

#### 4.3.1 Electrochemistry of Cubanes in Nonaqueous Solvents
In the original report by Das & coworkers describing the synthesis of the cubane Co₄O₄(py)₄(OAc)₄, 4.1, it was reported that 4-substituted pyridines could be used as a replacement for py in the cubane synthesis. This allowed for the creation of a series of cubanes with tunable electronic properties. A follow-up study demonstrated that the acetates could also be replaced by substituted benzoates, which highlighted the robustness of the synthetic procedure. By replacing electron donating substituents on the benzoates with electron withdrawing substituents, the reduction potential of the cubane could be anodically shifted by ~300 mV. These results indicated that as long as the ratio between cobalt, pyridine and a carboxylate was held at 1:1:2, the desired neutral cubane could be isolated following the oxidation of the mixture with H₂O₂. This strategy of pre-synthetic modification stands in contrast to the report by Christou of the post-synthetic modification of a related Co₄O₄ cubane, in which acetate ligands were exchanged with substituted benzoates by heating the cubane in refluxing MeCN in the presence of an excess of corresponding benzoic acid.

We became interested in further exploring both pre- and post-synthetic modifications of the neutral cubane, 4.1. These efforts were inspired by an SI figure in the paper by Scandola & coworkers which seemed to indicate that at very anodic potentials the cubanes like 4.1 could be oxidized to the Co(IV)₂Co(III)₂ state. We note that this is only a formal oxidation state, as the holes are likely distributed throughout the Co₄O₄ core. We synthesized at new cubane, Co₄O₄(py-OMe)₄(OPr)₄ 4.3, as a test case to explore the electrochemical properties of these cubanes at highly anodic potentials. We envisioned that combining the electron donating properties of methoxypyridine and the solubilizing properties of the propionate ligands would yield a cubane that would be amenable to studying via standard electrochemical techniques in a variety of organic solvents.

The CVs of 4.3 at multiple scan rates are shown in Figure 4.21. The reversible wave at E₁/₂ = 1.36 V vs. Fe⁺⁺/Fc, Figure 4.21a, indicates that the cubane could be oxidized to the
Co(IV)$_2$Co(III)$_2$ state, and it does not decompose, at least on the electrochemical time scale (i.e. $> 20$ seconds). Scan rate dependence experiments were then performed, Figure 4.21b, which showed that an increase in the peak-to-peak separation of this second oxidation wave. This suggest that the standard rate constant for this electron transfer is significantly smaller than that of the first oxidation wave, which remains electrochemically reversible up to a scan rate of 10 V/s. This result confirms that indeed this class of Co$_4$O$_4$ cubanes may be oxidized to the Co(IV)$_2$Co(III)$_2$ state. As discussed in section 1.3 of this thesis, this is the same oxidation state that is proposed to be active for formation of the O–O bond in Co-OEC.$^{47}$ However, it is unlikely, given the very reversible CV features in Figure 4.21, that significant bond breaking or bond formation occurs in 4.3$^{2+}$. The decrease in the standard rate constant of the second oxidation is consistent with an increased structural rearrangement following the removal of the electron, but it is most likely related to a small redistribution of ligand electron density that accompanies the stabilization of a second hole throughout the cubane.

**Figure 4.21** (a) CV of 1 mM 4.3 in MeCN using a gold working electrode and supporting electrolyte 0.1 M TBAPF$_6$. The two reversible waves are labeled. (b) Scan rate dependent CVs of 4.3 with the same electrochemical setup. The current has been normalized by dividing by $[\text{scan rate (V/s)}]^{1/2}$.
Due to the extremely high reduction potential for the second oxidation of 4.3, conditions have yet to be found that allow for the isolation of the cubane in this oxidation state. Very few chemical oxidants have reduction potentials high enough to drive this oxidation. For example, one of the strongest triarylamminium radical cations known, \([\text{N}([\text{C}_6\text{H}_4\text{Br}_3-2,4,6]_3)^+\), has only an equivalent reduction potential as \(4.3^{2+}\) (1.36 V vs. \(\text{Fc}^+/\text{Fc}\)).\(^{48}\) Bulk electrolysis methods were performed in both MeCN and DCM solvents to try to isolate this material, but due to the high solubility of the oxidized product, pure compound could not be isolated without significant contamination with excess supporting electrolyte. It is possible that a cubane substituted with aryl carboxylates, in combination with an appropriate electrolyte anion (\(\text{ClO}_4^\text{−}\) or \(\text{BF}_4^\text{−}\)) would create a sparingly soluble double salt in its \(\text{Co(IV)}_2\text{Co(III)}_2\) form, which would be amenable to isolation via selective precipitation following bulk electrolysis.

Despite the challenges with isolating the cubane in this highly oxidized state, we were able to compare its absorbance features with those of the singly oxidized and neutral

\[
\begin{align*}
\text{Co}_2\text{O}_2(\text{OPr})_4(\text{py-OMe})_2 & \rightarrow \text{Co}_2\text{O}_2(\text{OPr})_4(\text{py-OMe})_2^{+} \rightarrow \text{Co}_2\text{O}_2(\text{OPr})_4(\text{py-OMe})_2^{2+} \\
\text{Abs} & \text{Wavelength / nm} & \text{Abs} & \text{Wavelength / nm}
\end{align*}
\]

**Figure 4.22** (a) Absorption changes associated with the electrochemical oxidation of 4.3 (red) to 4.3\(^{+}\) (green). (b) Absorption changes associated with the electrochemical oxidation of 4.3\(^{+}\) (green) to 4.3\(^{2+}\) (blue). Inset: the difference spectra for the second oxidation.
complexes using spectroelectrochemistry. The results of the spectroelectrochemistry experiments on 4.3 are presented in Figure 4.22. In Figure 4.22a, the absorption changes associated with the oxidation of the neutral cubane to the singly oxidized cubane are shown, which features two isosbetic points at 316 nm and 391 nm. A second electrolysis at a potential past the second oxidation wave leads to the absorption changes shown in Figure 4.22b. Isosbetic points for this transformation were not observed, rather the spectrum is characterized by a general increase in absorbance across the visible spectrum. The difference spectrum, inset in Figure 4.22b, highlights the greatest changes in the spectrum, which occur between 300 – 400 nm. These results create a foundation for further characterization experiments, such as with advanced x-ray absorption methods, which would be of interest for understanding the precise distribution of the holes within the Co(IV)$_2$Co(III)$_2$O$_4$ core.

4.3.2 Pre- and Post- Synthetic Strategies for Coupling Cubanes with NMI Photooxidants

From the our studies on 4.1, described earlier in this chapter, we were aware that silica chromatography was a useful method for separately pure cubanes from Co(III)-based and Co(II)-based impurities. We envision that silica chromatography would likewise be useful for isolating a single, desired, cubane from a statistical mixture. The prospect of being able to selectively functionalize a single ligand on the cubane was attractive because it opened the possibly of covalently linking the cubane to a photooxidant, such as a 1,8-naphthalimides (NMIs). NMI have been extensively studied as imagining agents, organic LEDs, and sensors, due to their attractive photophysical properties, namely their propensity to undergo photoinduced electron transfer. Based on known electrochemical and fluorescent properties of NMIs, we predicted that the photoexcited singlet state of unsubstituted NMI could drive the oxidization of a Co(III)$_4$O$_4$ cubane, and possibly also a Co(IV)Co(III)$_4$O$_4$ to its doubly oxidized states.
Our initial strategy for covalently attaching an NMI employed a Sonogashira cross-coupling, in a similar manner as has been used to couple a ruthenium polypyridine complex to naphthalene bisimides.\textsuperscript{55} We envisioned that a cubane with a single halogen handle for coupling to an alkynyl-NMI would be ideal for implementing this strategy. Therefore, the statistical synthesis of Co\textsubscript{4}O\textsubscript{4}(OAc)\textsubscript{4}(py-OMe)\textsubscript{3}(py-Br), \textbf{4.4}, was pursued as shown in Scheme 4.1. Gratifyingly, the solubility properties of the two pyridines used in the synthesis were different enough that TLC of the crude product mixture showed the expected statistical mixture of products. Mass spectroscopy analysis indicated that the bromide substituent pyridines caused the cubane to elute more rapidly on silica as compared to the methoxy substituents. Compound \textbf{4.4} was then purified from the mixture of cubanes using a very gradual gradient of 1–5 \% MeOH in DCM using an automated flash column. Unfortunately, all subsequent attempts to use \textbf{4.4} as a cross coupling partner in a Sonogashira reaction were unsuccessful. In all experiments, a complex mixture of products was found in the crude reaction mixture, and TLC analysis showed multiple fluorescent spots, suggesting that the NMI conjugated pyridine was prone to dissociate from the cubane at the elevated temperature needed to perform the reaction. It is also possible that the reducing nature of the catalysts for the Sonogashira reaction, Pd(0) and Cu(I), make them incompatible with within the cubane due to its Co(III) ions.
Since it seemed that the pyridines were prone to dissociate from the Co₄O₄ cubane core, a second approach was pursue in which the NMI was linked to the cubane through an acetate ligand. To this end, we initially pursued a pre-synthetic strategy as illustrated in Scheme 4.2. As in the synthesis of 4.4, the crude reaction mixture contained a statistical distribution of NMI linked cubanes, from which the desired cubane, 4.5, could be purified using silica gel chromatography, albeit only after multiple columns. The solvent system that was found to give the best separation was H₂O in THF, and a gradual gradient from 0 – 4 % gave pure 4.5 as indicated by ¹H NMR and mass spectrometry. The yield was 2.6 %, though the purification conditions were not optimized.

In addition, we explored a post-synthetic strategy for covalently linking a NMI photooxidant. We reasoned that under solvothermal conditions the acetate groups could be exchanged via protonolysis, in a similar manner as described by Christou with a related cobalt cubane, as mentioned previously. Indeed, as illustrated in Scheme 4.3, the reaction
between 0.7 equivalents of NMI(CH$_2$)$_5$COOH with 4.1 at refluxing temperatures in deaerated MeCN, gave 4.6 in a 26% yield are purification. This method is preferable since not as much NMI is wasted in the synthesis, and the yield is higher by a factor of ten. It is possible that the improved yield for the post-synthetic strategy was due to the solubility properties of 4.6, which allowed for it to be separated more readily from unreacted 4.1 and other NMI conjugated cubanes. Nevertheless, going forward, it seems that this is the most straightforward and widely applicable of the two strategies.

4.3.3 Ultrafast photoinduced oxidation of Co$_4$O$_4$ cubanes

With compounds 4.5 and 4.6 in hand, we initiated a series of experiments to determine whether the covalently linked NMI species was capable of photooxidizing the cubanes. We envisioned that the rate constants for the charge separation (CS) and charge recombination steps would be sensitive to the length of the alkyl linker. We would expect that the electronic coupling coefficient between donor and acceptor, $H_{AB}$, would be smaller with the longer linker, which should retard the rate of electron transfer in both the forward and reverse directions.

Picosecond transient absorption (TA) spectroscopy of solutions of 4.5 at concentrations ~ 0.5 mM in MeCN revealed two prompt features at 415 nm and 474 nm following an excitation at $\lambda_{exc} = 325$ nm, Figure 4.23a. The assignment of these features was accomplished by comparing with TA spectra attained in control experiments using the photooxidant, NMI(CH$_2$)$_5$COOH without the cubane attached. In the absence of a sacrificial electron acceptor, the TA spectrum of photoexcited NMI(CH$_2$)$_5$COOH is characterized by the broad singlet state, $^1$NMI, absorption at 474 nm, Figure 4.24a, which decays to the longer lived triplet state within ~ 200 ps. In the presence of an excess of
triethylamine, an intense feature at 417 nm is observed, Figure 4.24b which is assigned to the radical anion, NMI$^\sim$. Since it is this same 417 nm band that is observed in Figure 4.23a, we can confirm that the photoexcitation of 4.5 leads to a charge transfer event. The rate constant for this process could not be determined however, since the absorption feature of the charge

Figure 4.23 (a) Picosecond TA spectrum of ~ 0.5 mM 4.5. The decrease of the spectral features is shown over the time window of 0 ps (purple) to 78 ps (brown) ($\lambda_{exc} = 325$ nm). (b) Single wavelength kinetics monitored at 415 nm. The decay curve (black line) fits to a mono-exponential expressions with a time constant of 14.1 ± 0.3 ps.

Figure 4.24 Picosecond TA of NMI(CH$_2$)$_3$COOH in MeCN (a) in the absence of trimethylamine at the indicated time delays. (b) and in the presence of excess trimethylamine at the indicated time delays.
transfer state appears too rapidly following the excitation laser pulse. Conversely, the charge recombination could be followed by single-wavelength kinetics at $\lambda = 415$ nm, Figure 4.23b. The disappearance of this signal could be fit to a mono-exponential expression with a lifetime of $14.1 \pm 0.3$ ps, which corresponds to a rate constant of $7.1 \times 10^{10}$ s\(^{-1}\).

<table>
<thead>
<tr>
<th>Table 4.2 Ground/Excited State Reduction Potentials of NMI</th>
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<tr>
<td>$E_{00}$</td>
</tr>
<tr>
<td>(1NMI*)</td>
</tr>
<tr>
<td>3.5</td>
</tr>
</tbody>
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\(^{a}\) Reported in eV. \(^{b}\) Potentials reported versus Fc+/Fc. \(^{c}\) Estimated due to the uncertainty in the reduction potential of NMI*.

<table>
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<th>Table 4.3 Driving forces for photoinduced ET (eV)</th>
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<tr>
<td>Compound</td>
</tr>
<tr>
<td>4.5 or 4.6</td>
</tr>
<tr>
<td>4.5(^{+}) or 4.6(^{+})</td>
</tr>
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\(^{a}\) Driving force for 1NMI to directly reduce oxidized cubane.

To rationalize the kinetics of the charge separation and charge recombination events, we measured the thermodynamic parameters of NMI that influence the driving force of these electron transfers. The reduction potentials for the NMI*/NMI and NMI/NMI\(^{-}\) couples were interrogated by cyclic voltammetry, Figure 4.25a. The reduction of NMI in MeCN was reversible at a scan rate of 100 mV/s, while the oxidation of NMI was irreversible, therefore the reduction potential of NMI*/NMI could only be estimated using the anodic peak potential. The singlet excited state energy, $E_{00}(1\text{NMI}^*)$, was also measured from the intersection of the normalized absorption and emission bands, Figure 4.25b. Table 4.2 presents these values and the calculated excited state reduction and oxidation potential (both reported as reduction potentials), whereas Table 4.3 presents the calculated ET driving forces. The reduction potentials for cubanes, needed for these
calculations, were taken from the couples $E^0(4.1^{2+}/4.1^+) = 1.48$ V and $E^0(4.1^+/4.1) = 0.32$ V (versus the Fc$^+/Fc$ reference). From this data, we can see that the driving force of charge recombination for 4.5 is greater than charge separation by 0.62 eV, which suggests that the recombination rate constant is slower because it resides in the Marcus inverted region. The results in Table 4.3 also suggest that $^1$NMI should be capable of oxidizing the cubane to its doubly oxidized form. The oxidized complex 4.5$^+$ has been prepared via chemical oxidation with Ce(IV), and preliminary TA results do indicate that a charge transfer state is produced following photoexcitation. However, at this time, the purity of this compound has not been established, due to difficulty in using chromatography as a purification method. Therefore, this result will remain preliminary until such time that we can exclude the influence of possible impurities on the TA spectral features.

The excited state energetics of compound 4.6 are the same as 4.5, so any difference in kinetics of charge separation or charge recombination can be attributed to the length of the alkyl linker and its influence on the electronic coupling between the NMI and the cubane. Photoexcitation of 4.6 at 330 nm leads to TA spectral features that are qualitatively similar to those of 4.5, Figure 4.26. However, single wavelength kinetic measurements at
\[ \lambda = 415 \text{ nm} \]

revealed a significantly slower charge recombination with a lifetime of \( 69 \pm 3 \) ps, corresponding to a rate constant of \( 1.45 \pm 0.06 \times 10^{10} \text{ s}^{-1} \). The very early time points (0 to 10 ps) were also examined to determine whether a growth of the charge transfer state could be observed. As shown in Figure 4.27a, indeed a growth could be resolved, which

\[ \tau = 69 \pm 3 \text{ ps} \]

Figure 4.26 (a) Picosecond TA spectrum of \(~ 0.5 \text{ mM} \ 4.6\). The decrease of the spectral features is shown over the time window of 0 ps (purple) to 180 ps (brown) (\( \lambda_{\text{exc}} = 330 \text{ nm} \)). (b) Single wavelength kinetics monitored at 415 nm. The decay curve (black line) fits to a monoexponential expressions with a time constant of \( 69 \pm 3 \) ps.

\[ \tau = 2.0 \pm 0.2 \text{ ps} \]

Figure 4.27 (a) Picosecond TA spectrum of \(~ 0.5 \text{ mM} \ 4.6\). The growth of the CS state at 415 nm is shown over the time window of 0 ps (purple) to 10 ps (brown) (\( \lambda_{\text{exc}} = 330 \text{ nm} \)). (b) Single wavelength kinetics monitored at 415 nm. The growth curve (black line) fits to a monoexponential expressions with a time constant of \( 2.0 \pm 0.2 \) ps.
when fit to a mono-exponential expression, yields a rate constant for charge separation of \(5.0 \pm 0.5 \times 10^{11}\) \(s^{-1}\). These results indicate that increasing the length of the alkyl linker from -(CH\(_2\))\(_2\)- to -(CH\(_2\))\(_5\)- decreases the rate of charge recombination by approximately a factor of five, and leads to a charge separation rate that can be measured using ultrafast transient absorption methods.

### 4.4 Conclusion and Future Outlook

The results presented section 4.2 demonstrate that without purification by silica chromatography, the Co(III) oxo cubanes can be contaminated with Co(II) impurities, which are responsible for the observed water oxidation activity reported for these molecules. We have shown that an EDTA addition experiment can be used to test for the presence of Co(II) and a \(^{31}\)P NMR experiment can be used for the Co(II) quantification; these experiments are more definitive than \(^1\)H NMR spectroscopy for identifying paramagnetic Co(II) impurities. Beyond Co(II) as an impurity, the use of any Co(II) complex should be assessed as an authentic WOC versus precursors for heterogeneous catalysts such as Co-OEC owing to the proclivity of Co(II) complexes to undergo rapid ligand substitution.\(^{56,43}\) We note that water oxidation activity of a catalysts should not depend on whether an anodic potential is supplied electrochemically or (photo)chemically for mechanisms involving outer sphere electron transfers. In instances where homogenous and heterogeneous O\(_2\) evolution experiments do not concur, it is appropriate to consider whether other species are responsible for catalytic activity. Also, when inspecting carbon-based electrode surfaces for the deposition of heterogeneous catalysts, care must be exercised in the choice of oxidizing potentials as extreme values can give rise to spurious current that is associated with CO\(_2\) evolution and electrode degradation as established by DEMS.

The lack of significant water oxidation activity for the 4.1 is suggestive of the need for a solvent accessible coordination site on the periphery of the metal cluster. The results
of chapter 3 of this thesis demonstrated that the syn-oriented terminal OH ligands of the Co-OEC edge site are key for catalysis. The cubanes, like 4.1, do not possess these open coordination sites, and because the metal ligand bonds in the oxidized cubane 4.1+ are inert due to the low-spin electronic structure of the CoIII and CoIV atoms, the complex is resistant to hydrolysis. This leads to a stable molecule, capable of being oxidized at extremely positive potentials (> 1.36 V vs. Fc+/Fc) to a formal oxidation state of Co(IV)2Co(III)2; but one that presents a barrier to the formation of terminal CoIV–O intermediate. Further research is needed to develop novel ligand architectures that can stabilize a Co4O4 core while also providing open coordination sites for water or hydroxide ligands capable of participating in redox-leveling PCET events.

A possible strategy for accomplishing this task is presented in Scheme 4.4, which uses the DPEN (see chapter 3, section 3.2.1) as the framework for a more elaborate chelating ligand. It is possible that with the incorporation of the correct functional group at the 2-position of the pyridyl arms (blue R groups in Scheme 4.4), a cubane may be stabilized with only a single face open for coordination by solvent molecules. It is not clear at this time precisely what chemical functionality should be incorporated on to the dipyridyl arms to achieve this goal, though molecular modeling may provide some guidance, especially with respect to the simple geometric constraints imposed by the angles between the faces of the cubane and the pyridyl arms. Importantly, since the pyridyl arms can be independently synthesized prior to attaching to the naphthyridine backbone,57 we expect that a wide variety of functional groups, such heterocycles, carboxylates, alkoxides, or

Scheme 4.4 Strategy for Incorporating Open Coordination sites into Co4O4 Cubane
alkyl amines could be integrated into the R group through the strategic adaptation of known synthetic procedures.\(^{58}\)

Finally, in the last section of this chapter, we have demonstrated that NMI is a promising candidate for the study of fixed-distance photoinduced ET using Co\(_4\)O\(_4\) cubanes as the electron donor. We have shown that the energetics of the NMI excited state push the charge recombination rate into the Marcus inverted region, which allows for the positive identification and observation of a charge separated state. Furthermore, by extending the length of the alkyl linker, we are able to significantly slow the rate of charge separation. Currently, this strategy for fixed-distance ET is being extended to the water soluble Christou cubane, Co\(_4\)O\(_4\)(OAc)\(_2\)(bpy)\(_4\)\(^{2+}\). We anticipate that with an NMI conjugated to the doubly charged Co\(_4\)O\(_4\)(OAc)\(_2\)(bpy)\(_4\)\(^{2+}\) it will be possible to study the photoinduced PCET reactivity of the cubane at acidic pHs, providing a complement to the bidirectional PCET experiments discussed in chapter 1.
4.5 Experimental Methods

4.5.1. General Considerations.

Co(NO$_3$)$_2$·6H$_2$O (Alfa Aesar), sodium acetate (Sigma-Aldrich), sodium propionate (Sigma-Aldrich), pyridine (Sigma-Aldrich), 4-methoxypyridine (Sigma-Aldrich), methyl isonicotinate (Sigma-Aldrich), ethylenediaminetetraacetic acid tetrasodium salt dehydrate (Sigma-Aldrich), Ru(bpy)$_3$Cl$_2$·6H$_2$O (Sigma-Aldrich), sodium persulfate (Sigma-Aldrich), β-alanine (Sigma-Aldrich), 6-aminocaproic acid (Sigma-Aldrich), 1,8-Naphtahalic anhydride (Sigma-Aldrich), and ammonium cerium(IV) nitrate (Sigma-Aldrich) were purchased and used as received. Buffer solutions were made from KH$_2$PO$_4$ (Mallinckrodt) using 18 MΩ cm distilled water from a MilliPore purification system.

Synthesis of crude Co$_3$O$_4$(OAc)$_4$(py)$_4$, crude 4.1, was performed according to the procedures of Dismukes$^6$ and Bonchio & coworkers$^7$. Synthesis of crude Co$_3$O$_4$(OAc)$_4$(py-COOMe)$_4$, crude 4.2, was performed according to the procedure of Das$^1$. Synthesis of N-(2-ethanoic acid)-1,8-naphthalenimide was performed according to the literature procedure.$^{49}$ Proton nuclear magnetic resonance ($^1$H NMR) spectra were acquired on an Agilent DD2-600 (600 MHz) or Varian instrument and chemical shifts are referenced to residual protium in the NMR solvent (HDO = δ 4.79, CDH$_2$CN = δ 1.94, CDHCl$_2$ = δ 5.32). Mass spectroscopic (MS) data were acquired on a Bruker micrO-TOF-QII LCMS ESI-TOF mass spectrometer in the positive ion mode. All mass spectra were externally calibrated with sodium formate. Elemental analysis was performed by Midwest Microlabs (Indianapolis, IN).

4.5.2 Purification and Characterization of 4.1 and 4.2.

Purification of the compounds 4.1 and 4.2 was performed on a Biotage Isolera One automated flash chromatography system using a mobile phase gradient of 2–10% methanol/dichloromethane. A typical loading ratio was 10 mg of crude material for 1 g of
silica. Samples were loaded onto the columns using a minimal volume of dichloromethane. Typical yields after purification were 40–50%.

4.5.3 Synthesis of Oxidized Cobalt Cubane, [\textbf{4.1}]PF\textsubscript{6}.

Purified \textbf{4.1} (75.5 mg, 0.0886 mmol) was dissolved in 10 mL of acetonitrile. In a separate vial, 1.1 eq of (NH\textsubscript{4})\textsubscript{2}Ce(IV)(NO\textsubscript{3})\textsubscript{6} (53.4 mg, 0.0974 mmol) was dissolved in 3 mL of acetonitrile. To a the stirring solution of \textbf{4.1} was added the Ce(IV) solution in a dropwise manner. The mixture darkened and was stirred at room temperature for 30 min. The mixture was concentrated under reduced pressure and redissolved in 8 mL of DI water. To this aqueous solution was added a solution of 452 mg of KPF\textsubscript{6} in 5 mL of DI water, which resulted in a precipitation of the product. This precipitate was filtered over a 5 µm nylon filter paper, washed with 10 mL of ice water, and then 20 mL of diethyl ether. The solid was dried under reduced pressure resulting in a dark green solid (66.4 mg, 0.0666 mmol, 75.1 % yield). \textsuperscript{1}H NMR of this sample in CD\textsubscript{3}CN exhibited paramagnetically broadened peaks: 10.10 (12 H), 6.63 (8 H), 6.16 (4 H), 2.68 (very broad, 8 H). Crystals suitable for X-ray diffraction from a synchrotron source were grown by vapor diffusion of diethyl ether into an acetonitrile solution of [\textbf{4.1}]PF\textsubscript{6}.

4.5.4 Synthesis and Purification of \textbf{4.3}

\textbf{4.3} was synthesized in the same manner as \textbf{4.1} except that NaOAc was replaced with NaOPr, and py was replaced with py-OMe. Purification of \textbf{4.3} was performed on a Biotage Isolera One automated flash chromatography system using a mobile phase gradient of 2–10% methanol/dichloromethane and silica stationary phase. A typical loading ratio was 10 mg of crude material for 1 g of silica. Samples were loaded onto the columns using a minimal volume of dichloromethane. \textsuperscript{1}H NMR (CD\textsubscript{3}CN): 8.09 (d, 8H), 6.68 (d, 8H), 3.83 (s, 12H), 2.27 (m, 8H), and 0.96 (t, 12H).

4.5.5 Synthesis and Purification of \textbf{4.4}
Co(NO$_3$)$_2$•6H$_2$O (1.45 g, 5.00 mmol, 1 eq.), py-OMe (381 µL, 3.75 mmol, 0.75 eq.), [Hpy-Br]Cl (243 mg, 1.25 mmol, 0.25 eq) and NaOAc (11.25 mmol, 923 mg, 2.25 eq) were added to a round bottom flask in 15 mL of MeOH and refluxed at 90 °C until homogeneous. Removed from heat long enough that the solution stopped refluxing, then very carefully added 30 % solution of H$_2$O$_2$ (2.5 mL, 25 mmol, 5 eq.) to the mixture. Refluxed the dark green mixture for 4 h at 90 °C. Cooled mixture to room temperature and concentrated to remove most of the MeOH. Extracted green material with 100 mL DCM. Dried with MgSO$_4$ and filtered. Purification: Concentrated DCM layer and ran a silica plug (350 mL of silica, with 5 % MeOH/DCM eluent) to remove Co(II) and Co(III) impurities from the statistical mixture of cubanes. Concentrated dark green band and found 770 mg of dark green solid. Then chromatography was performed using a 100 g SNAP column in conjunction with a Biotage Isolera One automated flash column system using a mobile phase gradient of 1–5% MeOH/DCM over 10 column volumes with a flow rate of 25 mL/min. Collected fractions at the center of the third major green band. $^1$H NMR (CD$_2$Cl$_2$): for an unknown reason, broad signals were observed. 8.36 (2H), 8.23 (6H), 7.28 (2H), 6.65/6.62 (6H), 3.91 (3H), 3.85 (6H), and 2.06 (12H).

4.5.6 Synthesis and Purification of 4.5

Co(NO$_3$)$_2$•6H$_2$O (1.45 g, 5.00 mmol, 1 eq.), py (402 µL, 5.00 mmol, 1.00 eq.), NaOAc (7.5 mmol, 1.02 g, 1.5 eq.), N-(2-ethanoic acid)-1,8-naphthalenimide (673 mg, 2.5 mmol, 0.5 eq.), and NaOMe (2.5 mmol, 135 mg, 0.5 eq.) were added to a 50 mL round bottom flask in 15 mL of MeOH and refluxed at 90 °C until homogeneous. The flask was removed from the oil bath long enough that the solution stopped refluxing. Then, in very careful and control manner a solution of 30 % H$_2$O$_2$ (2.5 mL, 25 mmol, 5 eq.) was added to the mixture. Refluxed the dark green mixture for 4 h at 90 °C. At the end of this time, the mixture was concentrated to remove the MeOH, and the aqueous layer was extracted into DCM. The organic layer was dried with MgSO$_4$, and filtered. Concentrated the DCM
extracted, and ran the residue material through a plug of silica with 10% MeOH/DCM to collect only the green bands. Concentrated and found 835 mg of green solid. Loaded in 20 mL DCM onto 500 mL of silica, which had been equilibrated with 100 % THF. Eluted with the following: 1000 mL (100 % THF), 1800 mL (1 % H2O/THF), 1000 mL (2 % H2O/THF), and finally 1000 mL (4 % H2O/THF). Collected the third green band. Concentrated then ran a quick silica column eluting with 10% MeOH/DCM to remove the BHT inhibitor that was present in the THF solvent used in the first column. Concentrated and found 35.1 mg (0.0331 mmol, 2.65 % yield) of green solid. 1H NMR (CD3CN): 8.50 (d, 2H), 8.40 (d, 8H), 8.32 (d, 2H), 7.79 (t, 2H), 7.58 (q, 4H), 7.10 (q, 8H) 4.23 (m, 2H), 2.65 (m, 2H), 2.01 (s, 6H), and 2.00 (s, 3H).

4.5.7 Synthesis and Purification of 4.6

4.1 (300 mg, 0.352 mmol, 1 eq.) and NMI(CH2)3COOH (73.0 mg, 0.246 mmol, 0.7 eq.) were added to a flask with 17 mL of MeCN. Sparged solution with N2 then refluxed at 95 C for 6 h under an N2 atmosphere. Concentrated mixture then loaded onto a silica column (300 mL of SiO2, equilibrated with 2 % MeOH/DCM) in 6 mL of 2 % MeOH/DCM. Eluted with the following: 600 ml (2 % MeOH/DCM) and then 2000 (4 % MeOH/DCM). There were two major green bands and the first of the two of these was collected. Concentrated and found 71.4 mg (0.0647 mmol, 26.3 % yield).

4.5.8 Single Crystal XRD

The structure of 4.1[PF6] (Figure 4.1) was collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device at 15 K. Radiation was supplied from a synchrotron source (0.41328 Å). Crystal was mounted on a glass fibre using Paratone N oil. Data were collected as a series of φ scans. Data were integrated using SAINT59 and scaled with a multi-scan absorption correction using SADABS. The structures were solved by intrinsic phasing methods using SHELXS-97 and refined against F² on all data by full matrix least squares with SHELXL-
All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model.

4.5.9 Electrochemical Methods.

All electrochemical experiments were recorded at ambient temperature with a CH Instrument 760D or 730C potentiostat. A BASi Ag/AgCl reference electrode was used for CVs in aqueous solution. CVs in nonaqueous solvents were performed in a N$_2$-atmosphere glovebox, using Ag wire pseudo reference in conjunction with a Fc external reference. In the cyclic voltammogram (CV) experiments the counter electrode was a Pt wire, while in the bulk electrolysis experiments a Pt mesh was used. In the CV experiments, 3 mm diameter glassy carbon working electrodes were used predominately as well as in specific experiments 2 mm diameter platinum and gold electrodes. These were cleaned by polishing on felt with 1 µm alumina followed by 0.3 µm alumina, and then sonication in 18 MΩ cm distilled water, rinsing with acetone and drying with compressed air. For the bulk electrolysis experiments, glassy carbon plate electrodes were used (25 × 5 × 1 mm). These electrodes were cut from a 25 × 25 × 1 mm plate (SPI Supplies) using a diamond saw. The FTO electrodes were cleaned by sonication in acetone followed by rinsing in 18 MΩ cm distilled water. Thin-layer UV–vis spectroelectrochemistry experiments were performed using a 0.5 mm path length quartz cell with an Ocean Optics USB4000 spectrophotometer and a DT-Mini-2GS UV–vis–NIR light source in conjunction with the CH electrochemical workstation.

4.5.10 Ru(bpy)$_3^{2+}$/persulfate Photochemical Oxidation

Photochemical experiments were performed using a 1000 W high-pressure Hg/Xe arc lamp (Oriel), with a beam passed through a water immersed 0.4 OD filter, a 400 nm long-pass filter, an iris, and a water-jacketed cuvette holder. The solution O$_2$ concentrations were measured using a fluorescence-based O$_2$ sensor (Ocean Optics) fitted with a FOXY probe. Calibration of the probe was performed using two points, ambient air, [O$_2$] = 253
µM, and after bubbling N₂ for 15 min, [O₂] = 0 µM. The probe was inserted through the cap of the cuvette using a perforated septa and needle. In the dark, a 2 mL photochemical sample was made from stock solutions of [Ru(bpy)₃²⁺] = 2 mM, [S₂O₈²⁻] = 70 mM, and [4.1] = 1.32 mM all in 0.1 M KP₄ buffer (pH = 7) using 0.5 mL, 1 mL, and 0.5 mL from the respective stocks, resulting in the final concentrations, [Ru(bpy)₃²⁺] = 0.5 mM, [S₂O₈²⁻] = 35 mM, and [4.1] = 0.33 mM. Nitrogen was bubbled through the sample for 15 min before being exposed to the beam. The samples were stirred vigorously throughout the irradiation period.

4.5.11 DEMS (Differential Electrochemical Mass Spectrometry).

DEMS experiments were conducted on a home-designed/assembled DEMS system that has a detecting limit of ~0.1 nmol. The DEMS system has been described in details in a previous publication. Briefly, the DEMS setup consists of two differentially pumped chambers (ionization chamber and analysis chamber) and a quadruple mass spectrometer (QMS 220 M1, PrismaPlus, Pfeiffer Vacuum). The main and analysis chambers were pumped by a Pfeiffer 65 L/s and a Varian 250 L/s turbomolecular pumps, respectively, which were backed by a rotary vane pump (DUO 10 M, Pfeiffer Vacuum). The PrismaPlus™ quadruple mass spectrometer was connected to the analysis chamber and equipped with electron multiplier/faraday cup dual detecting units. The time constant of the mass spectrometer was in the millisecond regime.

A special dual thin layer flow electrochemical cell made of Kel-F was connected to the ionization chamber via an angle valve for the DEMS experiment. The construction of this cell can be found elsewhere. There are two compartments: the upper one for electrochemical reaction and the lower one for mass spectrometric detection, which are connected through 6 capillaries. In the upper compartment, the working electrode was pressed against a ~100 mm thick Teflon gasket with an inner diameter of 6 mm. This leaves an exposed area of 0.28 cm² and results in an electrolyte volume of ~ 3 µL. In the lower
compartment, a porous Teflon membrane (Gore-Tex) supported on a stainless steel frit served as the interface between the electrolyte and vacuum. It was pressed against a ~100 mm thick Teflon gasket with an inner diameter of 6 mm. The Gore-Tex Teflon membrane had a mean thickness of ~ 75 μm, a mean pore size of 0.02 μm and a porosity of 50%. Two Pt wires at the inlet and outlet of the dual thin-layer flow cell, connected through an external resistance (0.2~3 MΩ), were used as counter electrodes. A Ag/AgCl electrode in saturated KCl solution, connected to the outlet of the DEMS cell through a Teflon capillary, served as reference electrode. The electrolyte flow was driven by the hydrostatic pressure in a supply bottle (flow rate 7–10 μL/s), which ensured fast transport of the species formed at the electrode to the mass spectrometric compartment, where the volatile products were evaporated into the vacuum system of the DEMS (time constant, ~1–2 s) through the porous Teflon membrane.

Electrochemical measurements during DEMS experiment were carried out with EG&G PAR Model 173 Potentiostat/Galvanostat, with an EG&G PAR Model 175 universal programmer to generate potential steps and triangular waveforms for cyclic voltammetry (CV). Electrochemical and mass spectrometric data were simultaneously recorded with a National Instrument DAQ board, using home-written data acquisition software in LabView. Freshly polished glassy carbon (GC) electrode was served as working electrode for all DEMS experiments. Typical CV profile was recorded from a 1 mM sample concentration in 0.1 M KPᵢ pH 7 solution between +0.40 V and +1.50 V. The potential was scanned at the scan rate of 10 mV/s in the positive direction and at least 3 cyclic scans were performed to get the stable cyclic voltammograms.

4.5.12 EPR Spectroscopy.

EPR spectra were recorded on a Bruker ELEXIS E-580 spectrometer equipped with a Bruker ER4122 SHQE-W1 resonator and an Oxford Instruments ESR 900 cryostat. All
experiments were collected using field modulation of 10 G at 100 kHz and 2 mW microwave power at a temperature of 70 K.

4.5.13 Co(II) Induced $^{31}$P NMR Line Broadening Analysis.

Phosphorous nuclear magnetic resonance ($^{31}$P NMR) spectra were acquired on Varian Mercury400 (400 MHz) spectrometer with chemical shifts referenced to a 85% H$_3$PO$_4$ standard. A calibration curve of [Co(II)] versus the line width of phosphate $^{31}$P NMR signal was created as follows. To a 1 mL NMR sample of 0.5 mM purified 4.1 in 0.2 M KP$_i$ (pH = 7), 10 µL aliquots of a 2.5 mM:2.5 mM aqueous Co(OAc)$_2$:pyridine solution were added. After each addition, a $^{31}$P NMR spectrum was acquired using enough transients to ensure sufficient signal to noise (Figure 7). The line width of the resulting $^{31}$P signal was measured using the “dres” command in the VNMRJ data acquisition program. The experiment was repeated twice more to obtain a standard deviation of the average, Figure 7b. The Co(II) concentration of the three batches of 4.1 were assessed by measuring the FWHM of 0.426 mg/mL solutions (0.5 mM, assuming 100 % purity) in 0.2 M KP$_i$ (pH = 7). Three samples were made from each batch and the average and standard deviation were calculated. [Co(II)] was then calculated using the equation derived from the linear regression in Figure 7b. Error was propagated in the usual way.63

4.5.14 Electron Microscopy of Electrode Surfaces.

Microscopy samples were prepared from a bulk electrolysis of a solution of 1 mM analyte in 0.2 M KP$_i$ pH = 7 buffer using GC plate electrodes described in the Electrochemical Methods section. The electrodes were masked with scotch tape to expose two 10 x 5 mm areas. The electrolysis was performed for 300 s under rapid (400 rpm) stirring for all samples. After completion of electrolysis, the electrodes were gently rinsed in 18 MΩ distilled water, air dried, and then dried under vacuum. Field emission scanning electron microscopy (FESEM) was performed with a Zeiss Supra55VP. The FESEM was operated at a beam voltage of 5 kV at a working distance of 8.5 mm with a 30 µm aperture.
and the InLens detector. Elemental quantification was determined at a beam voltage of 13 kV with an energy dispersive X-ray spectrometer (EDS from EDAX Inc.) using EDAX ZAF correction factors.

4.5.15 X-ray Photoelectron Spectroscopy (XPS).

The presence of cobalt oxide on glassy carbon electrode surfaces after anodization in solutions of crude and purified 4.1 as well as without added 4.1 was examined using a Thermo Scientific K-Alpha XPS system. Samples were illuminated with a monochromated Al Kα X-ray source (1486.6 eV energy and 0.85 eV line width) of 400 μm spot size. A low-energy (0 to 14 eV) electron flood gun was employed to mitigate surface charging. High-resolution spectra of the Co 2p\(^{1/2}\) and 2p\(^{3/2}\) peaks were collected from 750.5 to 832.5 eV using an energy step of 0.1 eV, dwell time of 50 ms, average of 20 scans, and a pass energy of 50 eV. All samples were calibrated to the C 1s (284.8 eV) peak.

4.5.16 Digital Electrochemical Simulations.

The simulated CVs were constructed using the software DigiElch (version 7). For data presented in Figure 4.7, the background subtracted experimental data was imported into the program along with the relevant experimental conditions, such as area of the electrode, 0.0706 cm\(^2\) (3 mm diameter) and the scan rate 0.1 V/s. A charge transfer couple was inputted into the fitting program with a nonvariable reduction potential equal to 1.054 V using the Butler-Volmer model of electrode kinetics with a transfer coefficient of \(\alpha = 0.5\). The fitting program was then allowed to vary standard rate constant, \(k_s\), and the diffusion coefficient, \(D\). A satisfactory fit for the reversible couple in the three experimental CVs shown in Figure 4.7 was found with the values \(k_s = 0.008\) cm/s and \(D = 4 \times 10^{-6}\) cm\(^2\)/s.

For the simulation presented in Figure 4.17, the five step mechanism that was input into the program is outlined in the figure. For all chemical species a diffusion constant of \(D = 1 \times 10^{-5}\) cm\(^2\)/s was assumed. The area of the electrode was set to 0.0706 cm\(^2\) (3 mm
diameter) and the scan rate was 0.1 V/s. The initial concentrations used in the simulation were [Co(II)L] = 1 mM and substrate, [S] = 55 M. For the charge transfer steps, a Butler-Volmer model of electrode kinetics was used with a transfer coefficient of $\alpha = 0.5$.

4.5.17 Picosecond Transient absorption (TA) spectroscopy

Picosecond transient spectroscopy was performed on a home-built system constructed around a Coherent Libra HE Ti: Sapphire Amplifier System. The Libra HE incorporates a Coherent Vitesse oscillator that serves as the seed laser for the system. The Vitesse includes the modelocked Ti:Sapphire oscillator cavity pumped by a Coherent Verdi, a continuous-wave diode-pumped green laser. The Libra system also includes a Coherent Evolution diode pump second harmonic Q-switched laser. The Evolution operates at a 1 kHz repetition rate and provides the pump power to the amplifier module. The Libra-HE has an average output power of 3.5 W and a pulse width of 50 fs. 99.5% of the 800 nm output wavelength is directed into a Coherent OPerA SOLO optical parametric amplifier with the remainder being focused into a calcium fluoride (CaF$_2$) substrate for continuum generation by. The majority of the 800 nm beam was used to generate the pump beam in the OPA. Time resolution was achieved by propagating the excitation beam along a computer-controlled 1.70 m optical delay line with 1 µm precision (Aerotech ATS 62150). The pump and probe beams were focused collinearly at the continuously stirred sample with beam diameters of $\sim$500 µm and $\sim$250 µm respectively. The power of $\lambda_{ex}$ was kept between 1-2µJ/pulse at the sample. Laser power was measured using either a Coherent J-25MB-HE meter coupled to a Coherent Labmax Top or an Ophir Laser Measurement Group ORION/PD Power Meter (PD300-UV-SIR-ROITS) fitted with an ORION head (#572775). A 2 mm quartz cuvette was used for all samples.

Transient absorption (TA) spectra were recorded at discrete times after excitation with 325 nm pump pulses. The spectrum was then resolved in the monochromator (ISA Instruments, TRIAX 320). For both full spectrum and single wavelength kinetic
measurements, signal light entering the spectrometer was dispersed by a 300 × 500 blazed grating onto a Princeton Instruments PIXIS 100B CCD camera calibrated using a mercury argon pen lamp. Resulting spectra were averages of three replicates of 2000 sequences consisting of the four combinations of pump and probe used to correct for ambient and emissive signals for each time point, averaged together. Single wavelength kinetics where obtained by averaging 20 nm spectral windows about the wavelength of interest for each time point. In house developed software written in Python was used for acquisition control.

4.5.18 Calculations related to electrochemical current in CVs of Purified 4.1 (Figure 4.7).

At high buffer concentrations, the current density (I) at a given overpotential (η) is related to the exchange current density (I₀) by the following equation:

\[
\log I = \log I_0 + \frac{F}{RT \ln 10} \eta
\]  

(1)

The exchange current density, however, depends on the thickness of the film, d, as has been extensively discussed.\(^65\) The film thickness, d, is related to the exchange current density (I₀) through the following equation and set of constants:

\[
I_0 = I_0^{max} \tanh \frac{d}{d_{opt}}
\]  

(2)

where \(I_0^{max} = 1.75 \times 10^{-10} A/cm^2\) and is the current density when \(d \to \infty\), and \(d_{opt} = 1440 \text{ nm}\), which is the optimal film thickness. From the data in Figure 4.7, we measure an average current density at 1.5 V of the last sweep at \(1.1 \pm 0.4 \times 10^{-4} A/cm^2\) (using the last sweep avoids error from background subtraction, which more significantly affects the first sweeps). From this value, we calculate \(d = 8.2 \times 10^{-7} \text{ nm}\) using Eqs. 1 and 2, above. The film thickness can be correlated to moles of cobalt deposited using data from the
experimental section of ref 37, which leads to the following linear equation (with y-intercept fixed at 0) that relates film thickness to mC/cm$^2$ of charge passed:

$$\frac{mC}{cm^2} \text{of Co deposition} = 0.148 \times d_f (\text{nm})$$  \hspace{1cm} (3)$$

which leads to a charge density of $1.2 \times 10^{-7}$ mC/cm$^2$. This value can be converted to moles of deposited cobalt atoms by considering the area of the electrode (0.0707 cm$^2$) and that each coulomb of charge equates to one cobalt atom. Thus, $9 \times 10^{-8}$ nmol of cobalt, deposited as Co-OEC, could lead to a current density of 0.11 mA/cm$^2$ at 1.5 V vs. Ag/AgCl.

To make a meaningful comparison between the above value for the amount of cobalt needed to account for the observed current density and the amount of cobalt added to the electrochemical cell in the form of 4.1, we must consider the amount of cobalt in the form of 4.1 that experienced the potential of the electrode surface, and not the entirety of the [4.1] in the CV cell. We can use the simulation software to attain a reliable estimate for this value by considering the concentration profile at 1.5 V vs. Ag/AgCl for the reversible couple, Figure 4.28. By integrating under the concentration profile for the oxidized species,

![Concentration profile of the simulated CV shown in Figure 4.8a at 1.5 V vs. Ag/AgCl. The hash marks indicates the integrated area of 4.85 nmol/cm$^2$ used to calculate how much cubane experienced the electrode potential during a linear sweep to 1.5 V.](image)

**Figure 4.28** Concentration profile of the simulated CV shown in Figure 4.8a at 1.5 V vs. Ag/AgCl. The hash marks indicates the integrated area of 4.85 nmol/cm$^2$ used to calculate how much cubane experienced the electrode potential during a linear sweep to 1.5 V.
we find that 4.85 nmol/cm$^2$ of 4.1 are oxidized to 4.1$^+$ over the course of a scan to 1.5 V, leading to 0.34 nmol of 4.1 once the area of the electrode is considered. Since there are four cobalt atoms per molecule of 4.1, this leads to a fraction of 4.1 that would need to fully decompose to Co-OEC as:

\[
\frac{9 \times 10^{-8} \text{ nmol Co atom}}{0.34 \text{ nmol } 4.1 \times 4 \frac{\text{nmol Co atom}}{\text{nmol } 4.1}} = 6.6 \times 10^{-8} = 66 \text{ ppb}
\]

If we assume that the small amount of current observed in the red traces of Figures 4.7b-d is due to true molecular water oxidation catalyst by 4.1, then it is possible to determine the turnover frequency (TOF) of the catalyst as follows. The average current density found at 1.5 V vs. Ag/AgCl for CVs of purified 4.1 on glassy carbon electrodes was 0.11 mA/cm$^2$ (red traces, Figures 4.7b–d). First, we assume that the entirety of this current is used for the four electron oxidation of H$_2$O to O$_2$ by the molecules of 4.1 that experience the anodic potential at the electrode surface. We can convert this value to a TOF, using Faraday’s constant and the value for [4.1] at the electrode surface, which, as discussed in the previous section, can be attained using the simulation software (Figure 4.23).

\[
0.11 \times 10^{-3} \frac{\text{C}}{\text{s} \times \text{cm}^2} \times \frac{\text{mol } e^-}{96485.3 \text{ C}} \times \frac{1 \text{ mol O}_2}{4 \text{ mol } e^-} = \frac{0.28 \text{ nmol O}_2}{\text{s}}
\]

\[
\text{TOF} = \frac{0.28 \text{ nmol O}_2}{\frac{4.85 \text{ nmol 1}}{\text{cm}^2}} = 0.058 \text{ nmol/s}
\]
### 4.6 Crystallographic Table

**Table 4.4** Crystal data and structure refinement for [Co$_4$O$_4$(OAc)$_4$(py)$_4$]PF$_6$, [4.1]PF$_6$

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$^a$ GOF = ($\Sigma w(F_o^2 - F_c^2)^2/(n - p)$)$^{1/2}$ where n is the number of data and p is the number of parameters refined.

$^b$ R1 = $\Sigma ||F_o - |F_c||/\Sigma |F_o|$.

wR2 = ($\Sigma (w(F_o^2 - F_c^2)^2)/\Sigma (w(F_o^2)^2)$)$^{1/2}$. 

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4.7 References


(63) Harris, D. C. Quantitative Chemical Analysis; W. H. Freeman: New York, 2003; Ch. 3.
