Exploring the Progress and Mechanisms of Hydrogen Evolution Catalyzed by Cobaloximes: A Comprehensive Review

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Abstract

In recent years, significant progress has been made in the development of cobalt diamine-dioxime complexes, which have emerged as promising molecular catalysts. These catalysts offer several advantages, including enhanced stability against hydrolysis and versatility in various reaction conditions. Through derivatization of the ligand at the hydrocarbon chain connecting the two imine functions, the cobalt diamine-dioxime catalyst can be conveniently coupled with surfaces or photosensitizers. This modification provides a more efficient approach compared to the original cobaloximes. Notably, the cobalt diamine-dioxime catalyst has demonstrated activity in H\textsubscript{2} evolution under fully aqueous conditions, both when immobilized onto electrode materials and in light-driven homogeneous conditions. These remarkable properties create opportunities for the construction of molecular-based photocathodes, serving as a critical component in dye-sensitized photoelectrochemical cells.

Keywords: Electrocatalysis, overpotential, solar energy, cobalt complex, hydrogen evolution
I. Introduction

Hydrogen evolution has emerged as a key area of research in the quest for sustainable energy sources. Cobaloximes, a class of cobalt-based catalysts, has garnered significant attention for their potential in catalyzing the production of hydrogen. Understanding the progress and mechanisms of hydrogen evolution catalyzed by cobaloximes is crucial for the development of efficient and sustainable catalytic systems. The pursuit of developing cost-effective and efficient catalysts for hydrogen (H\textsubscript{2}) evolution using abundant materials is a subject of considerable interest. Despite the abundance of solar energy reaching the Earth's surface, global energy demands do not align with the availability of sunlight alone. Efficiently harnessing and converting solar energy into a storable fuel source is crucial for meeting future energy requirements. In this context, researchers have been actively exploring renewable sources capable of fulfilling the anticipated energy demands, with solar-driven water splitting and H\textsubscript{2} production being a primary target. A key challenge in this endeavor is the discovery of a robust and efficient catalyst, composed of earth-abundant elements, for the reduction of protons into H\textsubscript{2}. Water splitting is highly desirable as it stores 4.92 eV when two H\textsubscript{2}O molecules are converted into two H\textsubscript{2} and O\textsubscript{2}. However, the complexity arises from the involvement of separate multielectron redox processes, namely a four-electron oxidation and a two-electron reduction, making the reaction challenging. Direct electron or hole transfers to H\textsubscript{2}O produce high-energy intermediates, necessitating the use of catalysts that can stabilize these intermediates, thus reducing the energy barrier for H\textsubscript{2} evolution. Extensive efforts are currently focused on designing efficient and environmentally friendly electrocatalysts that operate at low overpotentials. Notably, cobalt diglyoxime complexes have demonstrated the ability to produce H\textsubscript{2} from protic solutions at relatively modest overpotentials.\textsuperscript{1}
This comprehensive review aims to explore the progress made in the field of cobaloxime-based hydrogen evolution catalysis and provide an in-depth understanding of the underlying mechanisms. The review begins by introducing the fundamental principles of hydrogen evolution and the importance of cobaloximes as catalysts. It then delves into the various strategies and approaches employed to enhance the catalytic activity and stability of cobaloximes. Moreover, this review presents a comprehensive analysis of the progress made in bulk electrolysis experiments and the determination of reduction potentials, apparent rate constants, and diffusion constants for various cobaloxime complexes. It also discusses the thermodynamic aspects, such as equilibrium constants, associated with the reduction of acids by Co(I) complexes. Peter et al. conducted studies on cobalt complexes with diglyoxime ligands, specifically Co(dmgBF$_2$)$_2$(CH$_3$CN)$_2$ and Co(dpgBF$_2$)$_2$(CH$_3$CN)$_2$, as well as Co complexes of [Co(TimR)X$_2$]$_n^+$. These complexes were characterized crystallographically, and their electrocatalytic behavior for H$^+$ reduction in CH$_3$CN was observed within the potential range of -0.55V to -0.20V vs SCE. Winkler and Gray focused on investigating the kinetics and thermodynamics of active Co$^{II}$ catalysts to determine the most favorable pathway for electron transfer during H$_2$ evolution. Solis and Schiffer, on the other hand, demonstrated that effective catalysts for cobalt diglyoxime complexes, Co(dRgBF$_2$)$_2$, can be identified by altering the substituent R and measuring the pKa values and reduction potentials of each electron transfer step. Overall, this comprehensive review provides a comprehensive overview of the progress and mechanisms of hydrogen evolution catalyzed by cobaloximes. It serves as a valuable resource for researchers in the field, offering insights into the design and optimization of cobaloxime catalysts for efficient hydrogen production.$^{1,2}$
In recent years, there has been growing interest in the exploration of cobalt complexes as electrocatalysts for various important chemical reactions. Among these complexes, those containing BF₂-bridged diglyoxime or propane-bridged macrocyclic tetraimine ligands have shown great potential due to their unique structural and electronic properties. This paper presents an investigation of the electrochemical and electrocatalytic properties of a series of cobalt complexes incorporating these ligands. The electrochemical behavior of these cobalt complexes is examined using cyclic voltammetry, providing valuable insights into their redox properties and stability. By analyzing the obtained voltammograms, the reduction and oxidation potentials of the complexes can be determined, shedding light on their electrochemical reactivity and potential applications as catalysts. By studying the behavior of these complexes, the relationship between H₂ evolution activity and Co²⁺ reduction potentials was established. The authors provided electrochemical evidence supporting the formation of Co(III) hydride intermediates and proposed a potential mechanism for the H₂ evolution reaction. Notably, complex 1, Co-(dmgBF₂)(CH₃CN)₂, exhibited both H₂ evolution and oxidation activity, confirming its capability as a molecular catalyst with a low overpotential for H₂ evolution. Overall, this investigation of the electrochemical and electrocatalytic properties of cobalt complexes containing BF₂-bridged diglyoxime or propane-bridged macrocyclic tetraimine ligands offers a comprehensive understanding of their reactivity and potential applications in various electrochemical transformations. The results obtained from this study contribute to the development of efficient and sustainable electrocatalysts for important chemical reactions.
Electrochemical Systems

The electrocatalytic activity of Complex 1, Co(dpgBF2)2(CH₃CN)₂, and its derivative (referred to as 2 or dpg) for hydrogen (H₂) evolution in acetonitrile (CH₃CN) has been investigated. These cobalt complexes have shown promising catalytic properties in facilitating the production of H₂ through electrochemical reactions.² The electrochemical measurements revealed that the one-electron reduction of complex 1 was reversible and occurred at a potential of -0.55 V vs SCE in CH₃CN (as shown in Table 2). The results of these electrochemical studies have demonstrated that both Complex 1 and its derivative exhibit catalytic activity for H₂ evolution. The complexes displayed favorable electrochemical properties, such as appropriate reduction potentials and good stability under the reaction conditions.

Scheme 1. Complexes 1-3 is Cobalt Difluoroboryl-Diglyoximate³
The introduction of a strong acid led to the observation of noticeable catalytic currents near the Co$^{II/III}$ couple. As the acid concentration was increased, both the peak current and the peak position exhibited changes. Specifically, there was an increase in the peak current, accompanied by a slight positive shift in the peak position. This behavior is depicted in Figure 1, where the catalytic current eventually reached a plateau. These findings suggest that the presence and concentration of the acid play a significant role in modulating the catalytic activity of the system, highlighting the importance of acid-catalyzed reactions in the electrochemical behavior of the Co$^{II/III}$ couple. Notably, the catalytic potential remained unaffected by variations in acid concentration. Similar observations were made for complex 2. In the absence of a catalyst, the reduction of H$^+$ occurred at potentials more negative than -1.0V. A range of proton sources was investigated, including CF3COOH, p-toluenesulfonic acid monohydrate (TsOH·H2O), (p-cyanoanilinium)BF$_4$, and HBF$_4$·Et$_2$O. While HBF$_4$·Et$_2$O demonstrated substantially increased rates of H$_2$ evolution, the competitive degradation pathways of the catalyst severely limited overall reaction efficiencies.
Figure 1 illustrates the cyclic voltammogram obtained for complex 1 containing 0.1 M [nBu4N][ClO4] in a CH3CN solution, under different acid conditions. The black curve represents the voltammogram obtained in the absence of any acid, with a concentration of 0.3 mM for complex 1. The red curve corresponds to the addition of 1.5 mM TsOH·H2O, while the blue and green curves correspond to the addition of 4.5 mM and 9 mM TsOH·H2O, respectively. The scan rate employed was 100 mV/s, and a glassy carbon electrode was used for the measurements. The cyclic voltammogram provides valuable information about the electrochemical behavior and redox properties of complex 1 under different acid concentrations.

Figure 2 showcases the cyclic voltammogram obtained for a solution containing 0.6 mM of complex 2 in CH3CN, with the addition of 0.1 M [nBu4N][ClO4]. The black curve represents the voltammogram obtained in the absence of any acid, while the red curve corresponds to the presence of 9 mM TsOH·H2O. The scan rate used for the measurements was 100 mV/s, and a glassy carbon electrode was employed. This cyclic voltammogram provides insights into the electrochemical behavior and redox properties of complex 2 in the presence and absence of TsOH·H2O acid.

In Figure 3, the cyclic voltammogram is presented for complex 4a containing 0.1 M [nBu4N][ClO4] in CH3CN solutions. The black curve represents the voltammogram obtained in the absence of any acid, with a concentration of 0.15 mM of complex 4a. The red curve corresponds to the presence of 1.5 mM TsOH·H2O acid, while the blue curve represents the presence of 9 mM TsOH·H2O acid. The scan rate used for the measurements was 100 mV/s, and a glassy carbon electrode was employed. This cyclic voltammogram provides valuable information about the electrochemical response and behavior of complex 4a in the presence of different concentrations of TsOH·H2O acid.

Table 1. Key Findings from Bulk Electrolysis Experiments: A Comprehensive Summary.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Source of Proton</th>
<th>Catalyst Conc/mM</th>
<th>Acid Conc/mM</th>
<th>Volume /ml</th>
<th>Potential/ V vs SCE</th>
<th>Duration/ min</th>
<th>Charge / coulomb</th>
<th>H2 Faradic yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>HBF₃·Et₂O</td>
<td>0.9</td>
<td>20</td>
<td>100</td>
<td>-0.48</td>
<td>30</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>5b/5c</td>
<td>HBF₃·Et₂O</td>
<td>0.7</td>
<td>20</td>
<td>100</td>
<td>-0.48</td>
<td>30</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>4b/4c</td>
<td>TsOH·H₂O</td>
<td>0.8</td>
<td>22</td>
<td>100</td>
<td>-0.58</td>
<td>30</td>
<td>54</td>
<td>-100</td>
</tr>
<tr>
<td>4a</td>
<td>TsOH·H₂O</td>
<td>0.9</td>
<td>21</td>
<td>100</td>
<td>-0.58</td>
<td>30</td>
<td>49</td>
<td>-90</td>
</tr>
</tbody>
</table>

By substituting methyl groups with electron-withdrawing phenyl substituents, the formation of complex 2 resulted in a positive shift of approximately 65 mV in the CoII/I reduction potential to around -0.28 V vs SCE. Electrochemical catalysis was observed with HCl·Et₂O, (p-cyanoanilinium)BF₄, TsOH·H₂O, and HBF₃·Et₂O, while no catalysis was observed with CF₃COOH. The catalytic currents reached a plateau at higher acid concentrations. Investigations involving cobalt difluoroboryl-diglyoximes and related compounds (4a-6b scheme-2) with macrocyclic tetramine complexes revealed a correlation between catalytic activity (H₂ evolution)
and CoII/I potentials. Among the cobalt catalysts studied, complex 1, with the most negative CoIII reduction potential, facilitated H₂ evolution using the weakest acid CF₃COOH (pKa=12.7). On the other hand, complexes with more positive potentials, such as 2, 4a, and 4b, required stronger acids like TsOH·H₂O (pKa=8.0). Further, complexes 5a and 5b, with the most positive potentials, necessitated even stronger acids such as HBF₄·Et₂O (pKa=0.1). In the case of complexes that were more readily reduced than 5b (e.g., 6a and 6b), no catalysis was observed even with HBF₄·Et₂O as the acid. From these findings, it can be concluded that complexes with more negative reduction potentials exhibited higher catalytic rates for proton reduction with weaker acids compared to those with more positive reduction potentials. The CoII/I potentials are related to CoI basicities, as indicated by the increase in pKa values for metal hydrides as the CoII/I reduction potentials become more negative.

Table 2. Electrochemical Properties of Cobalt Complexes: Reduction Potentials, Apparent Rate Constants, and Diffusion Constants. ³

<table>
<thead>
<tr>
<th>complex</th>
<th>$E^0$(Co(III/II)) (V vs SCE)</th>
<th>$E^0$‘(Co(II/I)) (V vs SCE)</th>
<th>$K_{app}\times10^{2d}$ (M⁻¹s⁻¹)</th>
<th>$D\times10^{5e}$ cm²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>-0.55</td>
<td>7$\times10^4$</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>-0.28</td>
<td>2</td>
<td>0.14</td>
</tr>
<tr>
<td>4a</td>
<td>-0.06b</td>
<td>-0.38</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td>4b</td>
<td>NO</td>
<td>-0.35</td>
<td>3</td>
<td>1.2</td>
</tr>
<tr>
<td>5a</td>
<td>-0.03b</td>
<td>-0.25</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>5b</td>
<td>NO</td>
<td>-0.20</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>6a</td>
<td>0.03b</td>
<td>-0.15</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>6b</td>
<td>NO</td>
<td>-0.08</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

In the provided information, the following observations can be made:

a) An irreversible couple was observed.
b) A reversible couple was observed.
c) The phenomenon was not observed.
d) TsOH·H₂O was utilized as the proton source, and the rates were determined using the equation $iC = nFSCPo(DkCsO)1/2$, where $n = 2$ and $S = 0.07$ cm².
e) The diffusion constant was determined by simulating the cyclic voltammogram in the absence of acid.

In the investigated electrocatalytic systems, H₂ evolution took place at potentials slightly lower than the $E^0$(CoIII) values for the respective complexes. Consequently, the generation of Co(I) species was a prerequisite for H₂ production. This finding aligns with the work of Espenson and colleagues, who studied H₂ evolution using Co-(dmgBF₂)₂(H₂O)₂ as the catalyst, CrCl₂ as the

8
electron donor, and HCl(aq) as the proton source. Stopped-flow kinetics experiments conducted in that system led to the identification of an intermediate. Two potential mechanisms were proposed: one involving the protonation of the hydride ligand to generate H₂, and the other involving a bimetallic reaction between two Co(III) hydrides. A similar mechanism was proposed for the electrocatalytic H₂ evolution mediated by the catalysts 1-2 and 4a-5b, except in this case, the active Co(I) species was electrochemically generated. Scheme 3 illustrates the two possible reaction pathways for H₂ formation from a cobalt(III) hydride, as observed in the electrochemical proton reduction catalyzed by cobalt macrocyclic complexes.³

\[
\text{Electron Transfer:} \quad \text{Co(III)} + e^- \rightarrow \text{Co(II)} \quad E^{0'}(\text{Co}^{III/II}) \quad (2) \\
\text{Hydride Formation:} \quad \text{Co(II)} + e^- \rightarrow \text{Co(I)} \quad E^{0'}(\text{Co}^{II/I}) \quad (3) \\
\text{Monometallic Pathway} \quad \text{Co(III)-H} + \text{HA} \rightarrow \text{Co(III)-H} + \text{A}^- \quad K_s, k_4 \quad (4) \\
\text{Bimetallic Pathway} \quad \text{Co(III)-H} + \text{Co(III)-H} \rightarrow 2 \text{Co(II)} + \text{H}_2 \quad K_{s_5} k_5 \quad (5) \\
\text{Bimetallic Pathway} \quad 2\text{Co(I)} + 2 \text{HA} \rightarrow 2\text{Co(II)} + 2\text{H}_2 + 2\text{A}^- \quad K_{bi} \quad (6)
\]

The equilibrium constant for both the monometallic and bimetallic reactions can be determined by combining the measured potentials for the reductions of the Co^{III/II} and Co^{II/I} couples with the H₂ evolution potential.

\[
\begin{align*}
\text{Co(I)} + 2 \text{HA} &\rightarrow \text{Co(III)} + \text{H}_2 + 2\text{A}^- \quad K_{\text{mono}} \\
2\text{Co(I)} + 2 \text{HA} &\rightarrow 2\text{Co(II)} + \text{H}_2 + 2\text{A}^- \quad K_{\text{bi}}
\end{align*}
\]

Table 3 presents the calculated values for the equilibrium constants of both the

<table>
<thead>
<tr>
<th>acid</th>
<th>pK_{bi}</th>
<th>pK_{mono}</th>
<th>pK_{mono}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃COOH</td>
<td>1</td>
<td>-11.3</td>
<td>-11.3</td>
</tr>
<tr>
<td>HBF₄ Et₂O</td>
<td>1</td>
<td>26.4</td>
<td>13.7</td>
</tr>
<tr>
<td>TsOH·H₂O</td>
<td>1</td>
<td>10.8</td>
<td>-1.9</td>
</tr>
<tr>
<td>CF₃COOH</td>
<td>2</td>
<td>-7.8</td>
<td>-17.6</td>
</tr>
<tr>
<td>HBF₄ Et₂O</td>
<td>2</td>
<td>17.2</td>
<td>7.4</td>
</tr>
<tr>
<td>TsOH·H₂O</td>
<td>2</td>
<td>1.7</td>
<td>-8.1</td>
</tr>
<tr>
<td>CF₃COOH</td>
<td>4a</td>
<td>-4.4</td>
<td>-9.9</td>
</tr>
<tr>
<td>HBF₄ Et₂O</td>
<td>4a</td>
<td>20.6</td>
<td>15.2</td>
</tr>
<tr>
<td>TsOH·H₂O</td>
<td>4a</td>
<td>5.1</td>
<td>-0.34</td>
</tr>
</tbody>
</table>
monometallic and bimetallic reactions with CF₃COOH, TsOH·H₂O, and HBF₄·Et₂O.

Based on the aforementioned findings, it can be inferred that the significance of the monometallic pathway is primarily limited to scenarios involving very strong acids or complexes with a relatively negative Co³⁺/²⁺ potential. The kinetics of the bimetallic pathway can be elucidated by employing a steady-state approach, which leads to two distinct limiting rate laws. A related study conducted by Artero et al. ⁷ involved the digital simulation of cyclic voltammetry (CV) data and thermodynamic considerations, ultimately leading the authors to conclude that the bimolecular pathway dominates in the case of complex 1 under weak acid conditions in acetonitrile. Supporting evidence for the presence of a Co(III)-H intermediate was obtained through the observation of a nearly reversible Co³⁺-H/Co²⁺-H couple in complex 1. However, no reversible redox wave was observed for complex 2, while complexes 4a-b exhibited quasireversible behavior.

**Winkler and Gray’s work**

In an alternative study, the focus was on investigating the kinetics and thermodynamics of an active Co²⁺ catalyst. The main objective was to gain valuable insights into the barriers associated with the individual steps involved in the process of H₂ evolution. By analyzing the catalyst's behavior, the researchers aimed to understand the underlying factors that influence the efficiency and performance of the H₂ evolution reaction. This comprehensive examination of the catalyst's kinetics and thermodynamics provided valuable information that could contribute to the development of improved strategies and materials for efficient H₂ production. By uncovering the barriers and understanding the reaction mechanisms, this study aimed to advance the knowledge in the field of hydrogen evolution catalysis and pave the way for more effective catalyst design in
the future. During the catalytic process, a cobalt(III) hydride intermediate is generated by the Co(II) glyoxime complex. For this investigation, difluoroboryl-bridged Co(II)-diglyoxime complexes were utilized. The production of H₂ from Co(III)H can occur through either homolysis (depicted in Figure 4, red) or heterolysis (depicted in Figure 4, blue) of the Co(III)-H bond.

In Figure 4, two distinct reaction pathways are depicted for the catalysis of H₂ evolution by CoII complexes. The homolytic pathway (shown in red) involves the delivery of reducing equivalents (D) to CoII complexes, leading to the formation of CoI species. These CoI species are subsequently protonated to generate CoIIIH intermediates. In the homolytic pathway, two CoIIIH species undergo bimolecular reductive elimination, resulting in the production of H₂. On the other hand, the heterolytic pathway (shown in blue) involves the protonation of CoIIIH species, which leads to the release of H₂. In this pathway, the CoIII species is reduced back to CoII by D.

In order to initiate the reduction of CoII([Co(dpgBF2)2(CH3CN)2]) to CoI ([Co-(dpgBF2)2(CH3CN)])-, a laser flash-quench method was utilized in this study. This technique allowed for the precise and controlled initiation of the reduction process. Time-resolved spectroscopy was then employed to monitor and analyze the transient species that are formed during the reduction reaction. By using this spectroscopic technique, the researchers were able to observe and study the short-lived species involved in the reduction process. This approach provided valuable insights into the reaction kinetics and dynamics, allowing for a more comprehensive understanding of the reduction mechanism and the behavior of the intermediate species. The combination of the laser flash-quench method and time-resolved spectroscopy proved to be a powerful approach in investigating the reduction of CoII to CoI, contributing to the overall
understanding of the catalytic process. In this experimental approach, a photochemical method was employed using methyl viologen (MV$^{2+}$) to quench pulsed-laser excited [Ru-(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine). The transient absorption spectra were recorded, and the obtained data were analyzed by fitting the transient difference spectra using a linear combination of the three molar difference spectra. The transient spectra were fitted by applying a mathematical model, $\Delta A_{\text{fit}} = \Delta \varepsilon \times \alpha$, where $\Delta A_{\text{fit}}$ represents the fitted transient absorbance, $\Delta \varepsilon$ denotes the change in molar absorption coefficient, and $\alpha$ represents the concentration of the species of interest. The fitting process aimed to capture the kinetics of the system and provide a quantitative analysis of the experimental data.

\[
\begin{align*}
\Delta \varepsilon_1(\lambda) &= [\varepsilon_{\text{Ru}^{3+}}(\lambda) + \varepsilon_{\text{MV}}(\lambda) - \varepsilon_{\text{Ru}^{2+}}(\lambda) - \varepsilon_{\text{MV}^{2+}}(\lambda)] \\
\Delta \varepsilon_2(\lambda) &= [\varepsilon_{\text{Ru}^{3+}}(\lambda) + \varepsilon_{\text{Co}^{+}}(\lambda) - \varepsilon_{\text{Ru}^{2+}}(\lambda) - \varepsilon_{\text{Co}^{2+}}(\lambda)] \\
\Delta \varepsilon_3(\lambda) &= [\varepsilon_{\text{Co}^{3+}}(\lambda) + \varepsilon_{\text{Co}^{+}}(\lambda) - 2\varepsilon_{\text{Co}^{2+}}(\lambda)]
\end{align*}
\]

In order to depict the photochemical electron transfer (ET) reaction, scheme-4 was employed, which provided a framework to describe the kinetic trace measured at 730 nm, as shown in Figure-5. The decay of the excited state of [Ru(bpy)$_3$]$^{2+}$ was characterized by the rate constant $k_1$, which was determined through time-resolved luminescence measurements. To determine $k_2$, Stern-Volmer quenching analysis was employed, yielding a value consistent with previous reports. In order to simulate the kinetics of the system, a differential equation-based approach was utilized.
Scheme 4 provided a framework to describe the kinetic trace measured at 730 nm, as shown in Figure 5. In Figure 5, a kinetics trace is presented, depicting the behavior of the reaction system comprising 20 μM [Ru(bpy)₃][PF₆]₂, 3.5 mM [MV][PF₆]₂, 0.1 M NBu₄PF₆, 125 μM CoII. The trace is measured at λex = 480 nm and λobs = 730 nm, and the data is plotted on a logarithmic time scale. Additionally, the figure includes the simulated fit, which represents the modeled response of the system based on the experimental conditions.

Concentration profiles were generated to illustrate the temporal changes in the concentrations of each species. These profiles provided a visual representation of how the concentrations evolved over time during the electron-transfer reactions. The rate constants governing the electron-exchange reactions between CoIII and CoII, as well as CoII and CoI, were determined using the Marcus cross relation. This relation allows for the estimation of rate constants based on the energetics of the electron transfer process. Additionally, self-exchange rate constants were calculated for the CoIII-CoII and CoII-CoI reactions, providing insights into the rates at which these species undergo electron transfer with themselves. These rate constants were documented in Table 4. To account for both inner and outer sphere rearrangements that occur during the electron transfer process, the reorganization parameter (λ) was calculated. The λ value captures the extent of structural reorganization that accompanies the electron transfer event. By considering these self-exchange rates and reorganization parameters, a comprehensive understanding of the electron transfer kinetics and the associated rearrangements was achieved. The reorganization energy for
Co$_{\text{III}}$-Co$_{\text{II}}$ self-exchange was found to be 3.9 (±3) eV, while for Co$_{\text{II}}$-Co$_{\text{I}}$, it was significantly smaller at approximately 1.4 (±0.05) eV. The high reorganization energy associated with Co$_{\text{III}}$-Co$_{\text{II}}$ electron transfer suggests that the barrier for the reduction of Co$_{\text{III}}$ by D is higher compared to Co$_{\text{II}}$, resulting in a lower specific rate. The driving forces (-ΔG0) for the elementary steps are depicted in Figure 6. The barrier for electron transfer depends on both ΔG and λ. It was observed that the largest barrier is associated with the H$_2$ formation step. In the heterolytic route (curve b, Figure 4), H$_2$ is released upon protonation of Co$_{\text{III}}$H, leading to the generation of Co$_{\text{III}}$, which then needs to be converted to Co$_{\text{II}}$.

Regenerate response

Table 4. Co(dpgBF$_2$)$_2$(CH$_3$CN)$_2$ complexes reaction parameters

<table>
<thead>
<tr>
<th>Cross reaction</th>
<th>k$_{22}$ reaction</th>
<th>k$_{11}$ reaction</th>
<th>$\Delta$E(V)$^a$</th>
<th>$K_{12}$</th>
<th>$k_{11}(M^{-1}s^{-1})$</th>
<th>$k_{12}(M^{-1}s^{-1})$</th>
<th>$k_{22}$(caicd) (M$^{-1}$s$^{-1}$)</th>
<th>λ(eV)</th>
</tr>
</thead>
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<tr>
<td>7</td>
<td>Co$<em>{\text{III}}$/Co$</em>{\text{II}}$</td>
<td>MV$^{2+/+}$</td>
<td>0.76</td>
<td>1.16×10$^{13}$</td>
<td>5.4×10$^{10}$d</td>
<td>6.0×10$^{8}$</td>
<td>9.3×10$^{-7}$</td>
<td>3.97</td>
</tr>
<tr>
<td>6</td>
<td>Co$<em>{\text{III}}$/Co$</em>{\text{II}}$</td>
<td>[Ru(bpy)$_3$]$^{3+/2+}$</td>
<td>0.97</td>
<td>4.74×10$^{9}$e</td>
<td>2.0×10$^{9}$b</td>
<td>5.2×10$^{7}$</td>
<td>9.5×10$^{-8}$</td>
<td>4.19</td>
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<tr>
<td>4</td>
<td>Co$<em>{\text{II}}$/Co$</em>{\text{I}}$</td>
<td>MV$^{2+/+}$</td>
<td>0.18</td>
<td>1.24×10$^{3}$</td>
<td>5.4×10$^{10}$d</td>
<td>2.0×10$^{8}$</td>
<td>1.2×10$^{8}$c</td>
<td>1.38f</td>
</tr>
<tr>
<td>3</td>
<td>MV$^{2+/+}$</td>
<td>[Ru(bpy)$_3$]$^{3+/2+}$</td>
<td>1.73</td>
<td>5.52×10$^{8}$</td>
<td>2×10$^{6}$b</td>
<td>5.7×10$^{9}$</td>
<td>6.2×10$^{2}$</td>
<td>1.91</td>
</tr>
</tbody>
</table>

$^a$ Estimated uncertainty ±0.5 M$^{-1}$s$^{-1}$. $^b$ Estimated uncertainty ±0.05eV.

The thermodynamic driving force for the elementary H$_2$ formation step, ΔG$^{0}$3a, relies on the average values of $E^{0}[\text{Co}^{\text{III}/\text{II}}]$ and $E^{0}[\text{Co}^{\text{II}/\text{I}}]$ (relative to the proton reduction potential). This analysis reveals that the heterolytic pathway is highly unfavorable due to the unfavorable driving forces and barriers associated with the Co$_{\text{III}}$H reaction. In contrast, the analysis of barriers and driving forces for the homolytic and heterolytic reaction pathways of Co$_{\text{III}}$H indicates a preference for the homolytic route.
In Figure 6, an investigation of the thermodynamics associated with the homolytic and heterolytic pathways of hydrogen evolution, shedding light on the energy landscape and feasibility of these pathways as potential catalysts for efficient hydrogen production. The figure illustrates the role of the reductant (D) in both pathways. The thermodynamic profiles depict the energy changes associated with each step of the respective pathways, providing insights into the feasibility and driving forces of the hydrogen evolution process.  

Schiffer’s work

In this research, the investigator conducted an extensive analysis to determine the reduction potentials of CoIII/II, CoII/I, CoIII/IIG, and CoI/0, along with the pKa values of CoIIH and CoIIIH, for a range of diglyoxime substituents R on the cobaloxime catalyst Co(dRgBF2)2. By exploring the influence of various substituents on the electrochemical properties of the catalyst, valuable insights were gained into the structure-function relationship and the potential for tailoring the cobaloxime catalyst for enhanced hydrogen evolution. The results of these calculations are depicted in Figure 7.
Their research primarily concentrated on BF₂-bridged complexes due to their enhanced stability in acidic environments compared to H-bridged cobaloximes, as demonstrated in previous experimental findings. Throughout the study, they examined the free energy variations occurring along the reaction pathway. By employing density functional theory (DFT), they calculated the reduction potentials and pKa values of the complexes. These calculated values were subsequently correlated with the Hammett constant (σp), which represents the electron-donating or electron-withdrawing nature of the substituents (-R) attached to the cobaloxime. A comprehensive list of the substituents used in the study and their corresponding Hammett constants can be found in Table 5.

**Scheme 5** outlines three monometallic (A) and three bimetallic (B) pathways for cobaloxime catalysts. These pathways represent different mechanisms by which the catalysts facilitate the evolution of hydrogen. The
monometallic pathways involve a single cobaloxime catalyst species, while the bimetallic pathways involve the interaction of two cobaloxime catalyst species. Each pathway offers a unique set of reaction steps and intermediates, ultimately leading to the production of hydrogen. The scheme provides a comprehensive overview of the potential pathways that can be explored and studied for the design and optimization of cobaloxime catalysts.  

**Table 5.** Substituents and Associated Hammett Constants.  

<table>
<thead>
<tr>
<th>−R</th>
<th>σ_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>−CN</td>
<td>0.66</td>
</tr>
<tr>
<td>−CF₃</td>
<td>0.54</td>
</tr>
<tr>
<td>−Cl</td>
<td>0.23</td>
</tr>
<tr>
<td>−H</td>
<td>0.00</td>
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<tr>
<td>−C₆H₅</td>
<td>−0.01</td>
</tr>
<tr>
<td>−CH₃</td>
<td>−0.17</td>
</tr>
<tr>
<td>−OCH₃</td>
<td>−0.27</td>
</tr>
<tr>
<td>−OH</td>
<td>−0.37</td>
</tr>
<tr>
<td>−NH₂</td>
<td>−0.66</td>
</tr>
</tbody>
</table>

**Figure 9a** illustrates the influence of substituents R on the Co³/², Co²/¹, Co³/²H, and Co¹/⁰ reduction potentials. In this graph, a more negative value of σ_p corresponds to a more electron-donating substituent, while a more positive value indicates an electron-withdrawing substituent. This relationship arises from the ease of reducing the metal center in the presence of an electron-withdrawing group. To guide the design of catalysts, reduction potentials and pKa values can be utilized to construct a free energy diagram (**Figure 8**) for different mechanistic pathways, such as mono or bimetallic pathways. Notably, it was observed that the H₂ production step in all mechanisms becomes more thermodynamically favorable (exoergic) at lower Co-H pKa values and more negative reduction potentials. Therefore, it is crucial to modify the catalyst in a manner that maintains a minimal overpotential and acid strength, while ensuring the efficiency of the hydrogen production step is not compromised.  

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In Figure 8, thermodynamic free energy diagrams are presented for the monometallic pathways (1A, 2A, and 3A) involving CH3 substituents (represented by blue lines (b)) and CF3 substituents (represented by red lines (a)). The relative free energies for half-reactions associated with electron transfer were calculated in reference to the HA/H2 couple in acetonitrile. These diagrams provide valuable insights into the energetics of the different pathways and highlight the variations in free energy profiles based on the nature of the substituents. By analyzing these diagrams, researchers can assess the relative stability and feasibility of the various monometallic pathways and make informed decisions regarding the design and optimization of cobaloxime catalysts.9

In Figure 9, two sets of calculated values are presented. In (a), the reduction potentials Eo(CoIII/I), Eo(CoII/I), Eo(CoIII/IIH), and Eo(CoI/0) for Co(dRgBF2)2 are shown as functions of the Hammett constants corresponding to the substituents R, as listed in Table 1. These reduction potentials provide insights into the thermodynamic properties of the cobaloxime complexes and how they vary with different substituents. In (b), the calculated pKa values of CoIIH and CoIIIH are displayed. The pKa values are also correlated with the Hammett constants of the substituents. The correlation coefficients, represented by the squares of the coefficients of determination, are reported as 0.905, 0.980, 0.966, 0.963, 0.976, and 0.972, respectively. These correlation coefficients indicate the strength of the relationship between the pKa values and the Hammett constants, providing valuable information for understanding the influence of substituents on the acid-base properties of the cobaloxime complexes.9

The findings indicate that it is crucial to design the catalyst to operate as closely as possible to the reference potential of the HA/H2 couple in order to minimize barriers. The free energy diagram, encompassing all the mechanisms depicted in scheme-5, serves as a valuable tool for identifying
the thermodynamically favorable pathway. By comparing the diagrams obtained for different substituents, it becomes possible to derive insights for designing more effective cobaloxime catalysts. These insights enable the optimization of catalyst performance by tailoring the substituents to achieve a more favorable and efficient reaction pathway.  

**Conclusions**

The quest for new, efficient, and durable catalysts based on abundant elements for proton reduction to produce H\(_2\) represents a significant challenge. Extensive chemical and electrochemical investigations have been conducted to explore potential reaction pathways, while thermodynamic analyses have shed light on the barriers and driving forces of the elementary steps involved in H\(_2\) evolution. Notably, the homolytic pathway has been found to possess a lower barrier, thus offering promising prospects. The utilization of photochemical methods has further aided in the identification of intermediates within the reaction cycle. Moreover, through the analysis of substituent effects on proton reduction catalyzed by cobaloxime complexes, a direct correlation between reduction potential and pKa values has been established for various substituents. By comparing free energy diagrams corresponding to different substituents, valuable insights into the relative effectiveness of the catalysts have been obtained. Ongoing research in this field aims to discover even more promising catalysts, which could pave the way for the development of molecular-based photocathodes for dye-sensitized solar cells.

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**Declaration**

The authors have no competing financial interests to disclose.
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