Electrocatalytic Proton Reduction by a Dicobalt Tetrakis-Schiff Base Macrocycle in Nonaqueous Electrolyte

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ABSTRACT: A series of dicobalt complexes, Co2L22+ and Co2LAc+, where L is a N6O2 coordinating bis(phenolate) tetrakis-Schiff base ligand, have been synthesized and characterized via electrochemical and spectroscopic techniques. [Co2LAc](ClO4)s crystallizes in the monoclinic space group P21/c, and the structure reveals a highly distorted octahedral geometry for the CoII ions, which are bridged by an acetate with a Co–Co distance of 3.2 Å. Cyclic voltammetry (CV) of Co2L2+ and Co2LAc+ in anhydrous acetonitrile reveals large anodic/cathodic peak splitting for the CoII/III redox transitions and a multielectron wave for the CoI/II reductions. The CVs for Co2L2+ and Co2LAc+ were also compared to those of Zn2LAc+ and H4L2+, to identify the ligand-center oxidations and reductions. Addition of trifluoroacetic acid (TFA) or acetic acid (AcOH) to the electrolyte solutions of Co2L22+ results in an irreversible reduction wave that is consistent with electrocatalytic H+ reduction. The catalytic rate law shows a first order dependence on [catalyst] and a second order dependence on [acid]. Using TFA as the acid source, the electrocatalytic H+ reduction rate constant for Co2L2+ determined to be 138 M−1 s−1, while coordination of acetate slows the rate to 63 M−1 s−1 for Co2LAc+. Controlled potential electrolysis of Co2L2+ with AcOH generated H2 in 72–94% Faradaic efficiency as determined by gas chromatography. Initial studies suggest CoII as the catalytically active form of the complex. These complexes represent a new class of Co-based electrocatalytic H+ reduction catalysts that utilize a bimetallic active site.

INTRODUCTION

Over the past several decades, significant effort has been focused on the creation of molecular components for artificial photosynthesis systems that use sunlight to drive the splitting of water into O2 and H2. The most common approach to creating an artificial photosynthetic device involves the development of efficient and robust catalysts for each half-reaction of water splitting, the oxidation of water to O2 and reduction of H+ to H2.

Recently, there has been increasing interest in developing coordination complexes utilizing first row transition metals in electrocatalysts for H+ reduction. One such complex that has garnered significant attention from a number of research groups is the mononuclear series of cobaloxime complexes. These have been shown to electrocatalytically reduce H+ to H2 at relatively low overpotentials and moderate rates with a wide variety of acids. In addition, there have also been studies on photocatalytic H+ reduction using cobaloxime catalysts.Given the number of different research groups working on cobaloxime complexes and the wide range of conditions used to study them, it is not surprising that there is some debate on the mechanism for H+ reduction to H2. The three most common mechanistic cycles proposed for H+ reduction are the heterolytic pathways of H+ + CoII–H → H2 + CoII or H+ + CoIII–H → H2 + CoII, and the bimolecular homolysis pathway of 2CoIII–H → H2 + 2CoII. Several dinuclear nickel, iron, and nickel–iron complexes have been investigated for electrocatalytic H+ reduction, but surprisingly, very few dicobalt. To the best of our knowledge, few such examples have been reported, an octamethylene bridged bis(cobaloxime) dimer by Gray et al., pyridazine based dicobalt complexes by Peters et al., and bis(pyridyl)pyrazolato bridged di-Co(terpyridine) by Llobet, Fukuzumi, and coworkers. The latter complex has a Co–Co distance of 3.9 Å, and the authors proposed an H+ reduction mechanism involving the formation of [CoII] from [CoIII] and H2, followed by heterolytic attack by a second H+ to give H2. We have become interested in dinuclear tetrakis-Schiff base macrocycles as possible coordination complexes for water splitting reactions. In 1970, Robson showed that the [2 + 2] condensation of 2,6-diformyl-4-phenol with 1,2-diaminopropane can be templated by various first row transition metal dications, including CoII, to give a dinuclear N4O2 Schiff base...
macrocycle where the metal centers are approximately 3 Å apart. This method is also somewhat flexible, allowing the incorporation of different aminoalkane side groups, which changes the coordination environment of the two transition metal centers. For example, utilizing N-methyl-2,2′-diaminodiethylamine provides a N₆O₂ ligation sphere for the two metals, each in a highly distorted octahedral coordination environment.

The N₆O₂ ligation sphere of this macrocycle maintains the metal–metal distance at ∼3 Å and also provides two adjacent coordination spots for substrate binding. Based on the reported electrocatalytic H⁺ reduction activity of other dicobalt complexes mentioned above, we wondered whether a dicobalt tetrakis-Schiff base complex may also display such activity. Herein we describe the electrocatalytic reduction of H⁺ by two analogous dicobalt tetrakis-Schiff base complexes, Co₂LaCS₄⁺ and Co₂LaCS₄⁺, as H⁺ reduction catalysts in acetonitrile (MeCN) using trifluoroacetic acid (TFA) and acetic acid (AcOH) as H⁺ sources, where L represents the N₆O₂ Schiff base macrocyclic ligand and Ac denotes a bridging acetate. To provide a better understanding of the electrochemical and spectroscopic properties of these dicobalt tetrakis-Schiff base complexes, we also compared the analogous zinc and protonated versions of the catalyst, Zn₂LaCS₄⁺ and H₄LaCS₄⁺, respectively, which allow us to characterize the contributions from the ligand framework alone.

### RESULTS AND DISCUSSION

#### Synthesis and Characterization

The syntheses of Co₂LaCS₄⁺ and Co₂LaCS₄⁺ followed the M²⁺ templated [2 + 2] macrocyclic condensation reaction of Robson and co-workers (Scheme S1 in the Supporting Information). Co(ClO₄)₂, 4-tert-butyl-2,6-diformylphenol, and N-methyl-2,2′-diaminodiethylamine were added to methanol and refluxed under N₂, yielding [Co₂L][(ClO₄)₂]₄, where L is the bis(phenolate) tetrakis-Schiff base macroyclic ligand. Addition of one equivalent of sodium acetate to the reaction mixture yields [Co₂LaCS₄][(ClO₄)₂]. The completion of the [2 + 2] condensation reactions for Co₂LaCS₄⁺ and Co₂LaCS₄⁺ was verified by electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) mass spectrometry and Fourier transform infrared (FTIR) spectroscopy. FTIR spectra of Co₂LaCS₄⁺ and Co₂LaCS₄⁺ show expected peaks for C=N stretches (ν ≈ 1641 – 1629 cm⁻¹) (Figure S1 in the Supporting Information). Additionally, Co₂LaCS₄⁺ displays peaks for the bridging acetate ligand at νᵣ = 1577 cm⁻¹ and νₛ = 1440 cm⁻¹. The lack of C=O stretches at 1680 cm⁻¹ confirms complete conversion of the aldehyde groups of 4-tert-butyl-2,6-diformylphenol into Schiff bases. Chemical oxidation of Co₂LaCS₄⁺ with two equivalents of NOPF₆ in MeCN generates a diamagnetic sample as shown by ¹H NMR (Figure S2 in the Supporting Information), consistent with formation of low-spin Co³⁺₂L₄⁺. The molar magnetic susceptibility (μₛ) of Co₂LaCS₄⁺ in the solid state was measured at room temperature and found to be 5.32 μₛ. This value is lower than expected for ferromagnetically coupled high spin (CoII)₂ and is consistent with a weakly coupled antiferromagnetic spin state. Similar weak antiferromagnetic interactions between Co²⁺ ions have been observed for tetrakis-Schiff base macrocycles with N₆O₂ and N₄O₂ coordination environments.

#### X-ray Crystal Structure

The crystal structure of Co₂LaCS₄⁺ is shown in Figure 1. Table 1 includes crystallographic data and structural refinement parameters. Unfortunately, all attempts to crystallize Co₂LaCS₄⁺ were unsuccessful. Co₂LaCS₄⁺ crystallizes in the monoclinic space group P2₁/n with nearly identical unit cell dimensions as Zn(II) and Mn(II) analogues (Zn₂LaCS₄⁺ and Mn₂LaCS₄⁺).
The Co(II) centers holding them at 3.22 Å apart. Each of the Co(II) centers are in a highly distorted octahedral geometry with the bridging acetate group occupying the sixth coordination site. There is a slight asymmetry in the coordination environment around the two Co(II) centers, with one of the Co–N(amine) bonds elongated by 0.22 Å as compared to the other. The rest of the bonds in the primary coordination sphere are roughly symmetric. Most dinuclear tetraakis-Schiff base complexes with \( \text{N}_2\text{O}_2 \) type coordination environments result in a planar structure. In contrast, increasing the chelating ability of the macrocycle by introducing \( \text{NCH}_2 \text{CH}_2\text{N} \) into the ligand framework drastically distorts the geometry of complex, resulting in a twisted "butterfly-like" structure. 30–35,48

**Electronic Spectra.** The ground state electronic absorption spectra of \( \text{Co}_2\text{L}^2 \), \( \text{Co}_2\text{L}^4 \), \( \text{H}_4\text{L}^2 \), and \( \text{Zn}_2\text{L}^4 \) in MeCN are shown in Figure 2. The dinuclear tetraakis-Schiff base complexes exhibit three primary absorbance bands in the UV–visible region at ~215, 250, and 385 nm. Each of these bands is assigned to the \( \pi \rightarrow \pi^* \) transition from the tetraakis-Schiff base macrocycle ligand (i.e., phenolate and the ligand framework). 31,45,49,50 Because of the pronounced involvement of the \( \pi \) orbitals from the azomethine group in the lowest energy \( \pi \rightarrow \pi^* \) transition of the ligand framework, this band is sensitive to the charge on the metal ions. 30,51 A red shift to 434 nm is observed for \( \text{Zn}_2\text{L}^4 \) due to the high charge density as compared to the metal dications. 30 A weak transition is also observed at 570 nm highlighting the Co(II) \( d \rightarrow d \) transition for \( \text{Co}_2\text{L}^4 \) and \( \text{Co}_2\text{L}^4 \).

![Figure 2](image-url) Comparison of UV–visible absorbance spectra of \( \text{Co}_2\text{L}^2 \) (dark green), \( \text{Zn}_2\text{L}^4 \) (green), \( \text{Zn}_2\text{L}^4 \) (orange), and \( \text{H}_4\text{L}^2 \) (dark red) in MeCN. Inset: Enlarged view of the absorbance centered at 575 nm highlighting the Co(II) \( d \rightarrow d \) transition for \( \text{Co}_2\text{L}^4 \) and \( \text{Co}_2\text{L}^4 \).

Table 1. Crystallographic Data and Structural Refinement Parameters for \([\text{Co}_2\text{L}^4](\text{ClO}_4)_2\)(MeCN)$_{0.5}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>formula</td>
<td>( \text{Co}<em>6\text{H}</em>{105}\text{Co}<em>4\text{N}</em>{13}\text{O}_{16}\text{Cl}_2 )</td>
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<tr>
<td>fw</td>
<td>1739.33</td>
</tr>
<tr>
<td>cryst syst</td>
<td>monoclinic</td>
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<tr>
<td>space group</td>
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<tr>
<td>( a ) [Å]</td>
<td>12.290(3)</td>
</tr>
<tr>
<td>( b ) [Å]</td>
<td>15.936(4)</td>
</tr>
<tr>
<td>( c ) [Å]</td>
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<tr>
<td>( \beta ) [deg]</td>
<td>106.425(3)</td>
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<tr>
<td>( \gamma ) [deg]</td>
<td>90</td>
</tr>
<tr>
<td>( V ) [Å$^3$]</td>
<td>4032.43(18)</td>
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<tr>
<td>( Z )</td>
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</tr>
<tr>
<td>( T ) [K]</td>
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</tr>
<tr>
<td>( \lambda ) [Å]</td>
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</tr>
<tr>
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</tr>
<tr>
<td>( \mu ) (mm$^{-1}$)</td>
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</tr>
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<tr>
<td>no. of obs ([ I &gt; 2\sigma(I) ] )</td>
<td>7804</td>
</tr>
<tr>
<td>refl/param ratio</td>
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<tr>
<td>( R_1 ) [ ( I &gt; 2\sigma(I) ) ]</td>
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<tr>
<td>( wR_2 ) (all data)</td>
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<tr>
<td>( GOF^* ) on ( F^2 )</td>
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$R_1 = \left( \sum \frac{w|F_o|^2 - |F_c|^2}{w|F_o|^2} \right) \left( \sum w|F_o|^2 \right)^{-1}$

$GOF^* = \left[ \sum w(F_o^2 - F_c^2)^2 \right]^{1/2} / \left[ \sum wF_o^2 \right]^{1/2}

\( R_1 \) is the usual goodness of fit, \( R_2 \) is defined as $R_2 = \left( \sum w(F_o^2 - F_c^2)^2 \right) / \left( \sum w(F_o^2)^2 \right)$, and \( GOF^* \) is the goodness of fit on \( F^2 \).

Table 2. Selected Bond Distances (Å) and Angles (deg) for \([\text{Co}_2\text{L}^4](\text{ClO}_4)_2\)(MeCN)$_{0.5}$ from the X-ray Crystallographic Analysis

<table>
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<tr>
<th>Bond</th>
<th>Distance (Å)</th>
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<td>Co1–Co2</td>
<td>3.22</td>
</tr>
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<td>Co1–O1</td>
<td>2.0796(17)</td>
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<tr>
<td>Co1–O2</td>
<td>2.1422(17)</td>
</tr>
<tr>
<td>Co1–O4</td>
<td>2.0465(18)</td>
</tr>
<tr>
<td>Co1–N1</td>
<td>2.074(2)</td>
</tr>
<tr>
<td>Co1–N2</td>
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</tr>
<tr>
<td>Co1–N3</td>
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</tr>
<tr>
<td>Co2–O1</td>
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<tr>
<td>Co2–O2</td>
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<tr>
<td>Co2–N2</td>
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<tr>
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<td>2.358</td>
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<tr>
<td>Co2–N6</td>
<td>2.083(2)</td>
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<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
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<td>O2–Co1–O1</td>
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<td>O1–Co2–O2</td>
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<tr>
<td>Co2–O1–Co1</td>
<td>98.19(7)</td>
</tr>
<tr>
<td>Co1–O2–Co2</td>
<td>99.49(7)</td>
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</table>
oxidations.31,54–60 Reductive waves are also seen at −2.20 and −1.57 V for Zn2LAc+ and H4L2+, respectively, which are attributed to reduction of the imines.61

CVs of Co2LAc+ and Co2L2+ also show ligand-centered reductions at −2.28 V and oxidations at +1.22 V, the latter of which occur at higher potentials as compared to Zn2LAc+ and H4L2+.31,54–61 The corresponding oxidation waves for each of the CoII → CoIII/CoII redox couples are shifted significantly to higher potentials, resulting in relatively large peak splitting (ΔE ≈ 0.72 and 0.42 V). Confirming their couple redox processes, the cathodic peak at +0.02 is not observed unless the preceding anodic scan extends past the second oxidation wave (Figure S3 in the Supporting Information). The non-Nernstian behavior of these transitions indicates a high degree of reorganization from changes in the Co spin state and likely distortions of coordination environment.50,52 The CVs for Co2L2+ are similar to Co2L2+ with the CoII/CoIII reduction at −0.12 V and a multielectron wave at −0.83 V including the CoIII/CoII transition, but also display an additional cathodic wave at −1.88 V. Large ΔE for the CoII/CoIII and CoII/CoIII/CoII oxidations are similar to Co2L2+ at 0.82 and 0.51 V respectively. The scan rate dependence for each of the Co redox transitions for Co2LAc+ and Co2L2+ shows a linear increase of peak current with higher ν1/2, indicating a diffusion controlled solution species (Figure S4 in the Supporting Information).62

Returning to the cathodic waves at approximately −0.78 V for Co2L2+ and Co2LAc+ reveals a significantly higher charge as compared to other Co centered waves, suggesting a multielectron process. The charge associated with these multielectron waves shows a strong dependence on the starting potential and anodic end point of the previous scan, as shown in Figure S3 in the Supporting Information. When the CVs were reversed prior to oxidizing CoII to CoIII (anodic waves at ∼+0.42 V), the charge passed (from −0.68 to −1.18 V) decreased by approximately one-third for Co2L2+ and one-half for Co2LAc+. The multielectron nature of the cathodic wave from −0.78 to −1.18 V for Co2L2+ can be seen in higher scan rate CVs in Figure 4. The CVs of Co2L2+ obtained at relatively slow scan rates of 50 and 100 mV/s show a single broad cathodic peak from −0.78 to −1.38 V, whereas faster scan rates clearly show two distinct waves at −0.78 and −1.33 V. Comparison of the charge passed for the cathodic processes at the faster scan rates (600 and 1000 mV/s) when normalized to CoIII/CoII reduction at +0.02 V is consistent with a 2e− process at −0.78 V and 1e− at −1.33 V. Cathodic differential pulse voltammetry (DPV) scans of Co2L2+ also show multiple reduction waves in this potential range (Figure 4, top). In addition, when the DPV scan is initiated in the CoII redox state, the peak current at −0.78 V is reduced (Figure 4, top, black trace). Taken together, the combined cathodic peak from −0.78 to −1.38 V for Co2L2+ is assigned as three closely spaced single electron reductions of CoII/CoII/CoIII, CoII/CoIII, and finally CoII/CoII. We surmise that, following the electrochemically slow CoIII/CoII reduction process in Co2L2+, the resulting coordination environment (including solvent binding) and spin states of the Co3+ ions are more amenable to reduction to Co3+, resulting in the overlapping multielectron waves. The lack of a clear cathodic wave for the
Co$^{II}$/Co$^{III}$ redox process at slow scan rates could also be due to a competing chemical step following the formation of Co$^{III}$/Co$^{II}$ that does not lead to Co$^{II}$. At higher scan rates, the Co$^{III}$/Co$^{II}$ redox process is kinetically competitive, resulting in the appearance of the cathodic wave at $-1.33$ V. In the CVs of Co$_2$L$^{2+}$, the charge passed for cathodic peak at $-0.83$ V only accounts for a $2e^-$ process when normalized to the Co$^{II}$/Co$^{III}$ reduction at $-0.12$ V, consistent with Co$^{III}$/Co$^{II}$ and Co$^{II}$/Co$^{I}$ reductions. The additional cathodic wave at $-1.88$ V for Co$_2$L$^{2+}$ is assigned as the Co$^{III}$/Co$^{II}$ redox process. The presence of the coordinated acetate ion in Co$_2$L$^{2+}$ is sufficient to separate the Co$^{II}$/Co$^{III}$ and Co$^{III}$/Co$^{II}$ reductions, pushing the second reduction to $-1.88$ V.

**Electrocatalytic H$^+$ Reduction.** To explore the possibility of Co$_2$L$^{2+}$ to catalyze H$^+$ reduction, we investigated its electrochemical response in anhydrous MeCN using a glassy carbon working electrode with increasing concentrations of TFA ($pK_a = 12.7$ in MeCN) and AcOH ($pK_a = 22.3$ in MeCN) as H$^+$ sources.$^{65}$ The thermodynamic reduction potential of the acid $E^0(\text{AH}/\text{HA}^-)$ can be related its $pK_a$ via eq 1,

$$E^0(\text{AH}/\text{HA}) = E^0(\text{H}^+/\text{H}_2) - 0.23(RT/F)pK_a(\text{HA})$$  \hspace{1cm} (1)

Roberts and Bullock recently measured the standard reduction potential of H$^+$ in acetonitrile, $E^0(\text{H}^+/\text{H}_2)$, via open circuit potential measurements and determined it to be $-0.028 \pm 0.008$ V vs Fe$^{3+/2-}$.$^{64}$ At standard conditions, $E^0(\text{AH}/\text{HA}^-)$ would be $-0.78$ and $-1.35$ V vs Fe$^{3+/2-}$ for TFA and AcOH respectively, but at high concentrations of the acid alone (unbuffered), homocoupling leads to an increase in effective acidity and a lowering of the standard reduction potential.$^{64-66}$

CVs of Co$_2$L$^{2+}$ in the presence of increasing amounts of TFA show an irreversible catalytic reduction wave starting at about $-1.28$ V (Figure 5a), which is close to the potential for the Co$^{III}$/Co$^{II}$ redox couple of Co$_2$L$^{2+}$ (see discussion above). This effect is more discernible in DPV scans of Co$_2$L$^{2+}$ in the presence of increasing TFA (Figure S5 in the Supporting Information), where the reduction wave initiates at the same potential as the Co$^{III}$/Co$^{II}$ redox couple. The magnitude of this catalytic wave in Figure 5a is significantly higher than the Faradaic responses of the Co$^{III}$/Co$^{II}$, redox processes at $-0.78$ V, which remain largely unchanged at different TFA concentrations. The current evolved during this irreversible cathodic wave is directly proportional to the concentration of TFA in the electrolyte, which is consistent with electrocatalytic H$^+$ reduction.$^{19,61,67-70}$ The waves also exhibit a plateau at about $-1.88$ V, indicating that the catalytic reaction is sufficiently rapid that the current is partially controlled by diffusion of H$^+$ to the electrode surface.$^{20,71,72}$ The potential at $i_{cat/2}$ ($E_{cat/2}$) at $5$ mM and $55$ mM TFA was $-1.58$ V and $-1.66$ V respectively.

The catalytic peak current ($i_c$) at $-1.88$ V for H$^+$ reduction was observed to vary linearly with [TFA], suggesting a second order rate dependence. Furthermore, $i_c$ also varied linearly with [Co$_2$L$^{2+}$], indicating a first order dependence in catalyst (Figure 6). This is consistent with electrocatalytic H$^+$ reduction, suggesting that under these conditions the catalytic peak current ($i_c$) is related to the concentration of the catalyst and acid by eq 2,$^{62,67}$

$$i_c = n FAC \sqrt{Dk[H^+]^2}$$  \hspace{1cm} (2)

where $n_c = 2$, the number of electrons involved in the catalytic process, $F$ is the Faraday constant, $A$ is the electrode surface.
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area, C is the catalyst concentration, k is the catalytic rate constant, and D is the diffusion coefficient of CoL2+TFA. For a noncatalytic redox wave in CV scans obeying Nernstian behavior, the Faradaic peak current (ip) follows the Randles–Sevick equation62

\[ i_p = 0.4463n_F A C nD/RT \]

where \( n_F \) = number of electrons involved in the redox process, \( v \) is scan rate, \( R \) is the universal gas constant, and \( T \) is temperature (K). Comparing the ratio of catalytic (ic) to noncatalytic (ip) currents via eq 4 allows for the straightforward determination of the electrocatalytic rate without prior determination of D.

\[ \frac{i_c}{i_p} = 2.242 \frac{n_F}{n_p} \sqrt{\frac{kRT[H^+]}{n_Fv}} \]

Due to the absence of an ideal one electron redox process for CoL2+, we have used the CoII/III reduction at 0.08 V as a one electron noncatalytic peak (ip) to obtain an approximate k from eq 4.73,74 Since this is an electrochemically nonreversible oxidation, the value of ic is likely smaller than that of a reversible oxidation. Consequently, the rate obtained from this analysis may be higher than the actual rate. This analysis was developed for catalytic systems following a simple EC mechanism; however, numerous groups have applied this methodology to more complicated catalytic systems, allowing them to compare catalytic rates for a range of complexes.20,67,69,75 The catalytic rate constant (k) obtained for CoL2+ by comparing the ratio of ic/ip over a range of scan rates (v) (Figure S6 in the Supporting Information) is \( \sim 138 \) M\(^{-2}\) s\(^{-1}\).

A similar electrocatalytic study was performed with CoLAc+ to investigate the effect of acetate coordination and potential inhibition of H+ reduction. As shown in Figure Sb, CVs of 1 mM solution of CoLAc+ in the presence of excess TFA showed an electrocatalytic wave close to that of the CoII/CoI redox couple, similar to CoL2+. The electrocatalytic waves are shifted to more reducing potentials than that of CoL2+ and are preceded by a shoulder at \(-1.58 \) V. The shift in catalytic current to more reducing potentials, as compared to CoL2+, is likely due to activation of the complex for H+ reduction via acetate dissociation at the potential for CoII/CoI reduction.

Similar to CoL2+, the catalytic peak current (ic) at \(-2.0 \) V was found to have a second order rate dependence on [TFA] and first order in [CoLAc+] (Figure S7 in the Supporting Information). The catalytic rate (k) obtained from eq 3 for CoLAc+ (Figure S8 in the Supporting Information) is \( \sim 63 \) M\(^{-2}\) s\(^{-1}\). This rate is slightly lower than that of CoL2+, suggesting that acetate dissociation is a limiting factor on the electrochemical time scale.

The electrocatalytic response of CoL2+ was also compared to background signals from the glassy carbon electrode under similar conditions. CVs of CoL2+ show a significantly higher current and lower onset potential for the electrocatalytic wave as compared to CVs of the bare electrode at three different concentrations of TFA (Figure S9 in the Supporting Information). Additionally, to eliminate the possibility of a pseudocatalytic current arising from heterogeneous Co species deposited on electrode during the electrocatalytic scans, we removed the electrode after scanning CoL2+ in the presence of 5 equiv of TFA and placed the same uncleaned electrode in fresh electrolyte (without CoL2+) with and without 5 equiv of TFA. The repeated CV scans of the uncleaned electrode show similar currents to background, suggesting that the initial electrocatalytic waves for CoL2+ are due to homogeneous H+ reduction (Figure S9 in the Supporting Information).

The electrocatalytic activity of CoL2+ was also investigated using AcOH as the H+ source (Figure 7). CVs of CoL2+ with increasing concentration of AcOH displayed similar electrocatalytic waves to those with TFA, initiating at \(-1.28 \) V and reaching a peak at \(-1.88 \) V. \( E_{onset} \) for CoL2+ with 5 mM and 55 mM AcOH was \(-1.68 \) V and \(-1.66 \) V respectively. The catalytic current at \(-1.88 \) V showed linear first order dependence on [AcOH] (Figure S10 in the Supporting Information) and a second order dependence on [CoL2+] at constant acid concentrations (Figure S11 in the Supporting Information). AcOH being a weaker acid than TFA, the onset potential for reduction of AcOH at the bare electrode is expected to be at a lower potential than TFA. This is manifested when we perform electrocatalysis at an uncleaned electrode (removed after scanning CoL2+ in the presence of 5 equiv of AcOH). With the unclean electrode placed in fresh electrolyte without CoL2+, with and without 5 equiv of AcOH, we observed very negligible current at \(-1.88 \) V (Figure S12 in the Supporting Information). In addition, the catalytic current (ic) reaches a limiting current at high H+ concentration (>400 mM TFA and >1000 mM AcOH) (Figure S13 in the Supporting Information). These results with both TFA and AcOH as the proton source support our hypothesis of homogeneous H+ reduction using CoL2+.

In order to characterize the product of electrocatalysis, controlled potential electrolysis (CPE) of 1 mM CoL2+ was carried out at \(-1.88 \) V in the presence of 100 mM AcOH in MeCN, with stirring in a sealed flask sparged with N2 (Figure S14 in the Supporting Information). A piece of carbon paper was used as the working electrode and gave a nearly identical CV for CoL2+ as those shown in Figure 3 and Figure 5. The head space above the electrolyte solution was examined by gas chromatography (GC) at various time points throughout the CPE, and H2 was detected in 72–94% Faradaic efficiency (Figure S14 in the Supporting Information).

Interestingly, the onset potential and peak potential for the H+ electrocatalytic reduction wave for CoL2+ were the same.
irrespective of these acids, which suggests a similar mechanism. The electrocatalytic wave initiates at the tail of the multi-electron wave where Co$_2$ is formed (see discussion above), $\sim -1.28$ V. This suggests that the formation of [Co$_2L_2$]$^0$, or its redox equivalent, is required to initiate H$_2$ production. The 3.22 Å Co–Co distance seen in the crystal structure of Co$_2$LAc$^+$ is likely too long to involve a bridging hydride as most known Co(N–H) have Co–Co distance in the range of 2.2–2.3 Å.\textsuperscript{76,77}

One potential pathway consistent with the electrocatalytic wave initiating at $-0.9$ V would involve the sequential two electron reductions and protonations of [Co$^{II}$Co$^{III}$] to generate [Co$^{II}$HCo$^{III}$H$_2$], which could then undergo intramolecular homolysis to give [Co$^{III}$Co$^{II}$] and H$_2$. This pathway differs from that of the dicobalt complex of Llobet, Fukuzumi, and co-workers which only requires reduction to the [Co$^{III}$Co$^{II}$] state and protonation to give [Co$^{III}$Co$^{III}$H$^-$], which subsequently undergoes heterolytic attack by a second H$^+$ to generate H$_2$.28 Alternatively, reduction of Co$_2$L$^+$ to [Co$^{II}$Co$^{III}$] could generate [Co$^{III}$Co$^{II}$H$^-$] in the presence of H$.$. Subsequent reduction to [Co$^{IV}$Co$^{II}$H] may be favored over [Co$^{IV}$Co$^{III}$H$^-$], which could then be followed by heterolytic attack by a second H$^+$ to generate H$_2$. Both of these pathways would be consistent with electrocatalytic wave starting at $-1.28$ V that is first order in [catalyst] and second order in [acid], but further examination will be required to clarify the exact process.

The electrochemical response of Zn$_2$LAc$^+$ in the presence of TFA was also investigated as a control study, as the central redox inactive Zn$^{II}$ ions are not expected to participate in H$_2$ reduction. In the absence of acid, Zn$_2$LAc$^+$ displayed a reduction wave at $-2.18$ V. Upon addition of TFA, a large irreversible reduction begins to appear at $-1.53$ V, similar to what is observed for H$_2$L$^2$+. The peak current for this cathodic wave reaches a plateau at 17 mM TFA and is consistent with demetallation of Zn$_2$LAc$^+$ leading to in situ formation of H$_2$L$^2$+ (Figure S15 in the Supporting Information). This is further supported by UV–visible absorbance changes of Zn$_2$LAc$^+$ in the presence of TFA (vide infra). Each of the tetrakis-Schiff base macrocycles have four imine (C–N=) bonds that are susceptible to reductive hydrogenation in the presence of acid, which may result in the appearance of a pseudocatalytic wave as reported by Saveant for a tris(glyoximato) cobalt complex.\textsuperscript{61}

While the irreversible reduction waves for Zn$_2$LAc$^+$ reached an asymptotic upper limit (Figure S15 in the Supporting Information), the electrocatalytic waves for Co$_2$L$^2$+ and Co$_2$LAc$^+$ continue to increase with TFA concentration higher than H$^+$ equivalents required for imine reduction (Figure 6). Finally, to investigate the stability of the Schiff base complexes in the presence of excess acid, we monitored the change in absorbance for Co$_2$L$^2$+, Co$_2$LAc$^+$, and Zn$_2$LAc$^+$ in anhydrous MeCN with subsequent additions of 65 equiv of TFA (Figure S16 in the Supporting Information). We observed insignificant changes in absorbance for Co$_2$L$^2$+ and Co$_2$LAc$^+$ after several hours, suggesting that the compounds stay intact in the presence of excess TFA. Zn$_2$LAc$^+$, on the other hand, showed a rapid red shift of the peak at 385 to 430 nm, suggesting that Zn$_2$LAc$^+$ undergoes demetallation. The stability of Co$_2$L$^2$+ and Co$_2$LAc$^+$ in the presence of 65 equiv of TFA was validated by MALDI MS (Figure S16 in the Supporting Information), showing M$^+$ ion peaks at m/z 803.98 for both the complexes, which indicates CF$_3$COO$^-$ adduct formation. We observe a less intense peak at m/z 632.1, corresponding to the loss of one Co from Co$_2$L$^2$+ and Co$_2$LAc$^+$. In contrast, for Zn$_2$LAc$^+$ we observed M$^+$ peaks only at m/z 637.05 and 575.10 corresponding to loss of one and two zinc atoms respectively from Zn$_2$LAc$^+$, as expected. It is worth noting that no parent ion peak at m/z 759.2 corresponding to Zn$_2$LAc$^+$ was observed. This is consistent with our hypothesis of demetallation of Zn from electrocatalysis of Zn$_2$LAc$^+$ in the presence of TFA, whereas Co$_2$L$^2$+ and Co$_2$LAc$^+$ remain stable over the course of several hours.

**CONCLUSION**

The results from this study show that a new class of dicobalt tetrakis-Schiff base complexes, Co$_2$L$^2$+ and Co$_2$LAc$^+$, are capable of electrocatalytic H$^+$ reduction in anhydrous MeCN using both TFA and AcOH as proton sources. CPE electrolysis of Co$_2$L$^2$+ with AcOH generated H$_2$ in 72–94% Faradaic efficiency. Despite the relatively high overpotential required to drive catalysis, this class of complexes gives us a chance to explore different dinuclear sites for catalytic H$^+$ reduction. Electrocatalytic H$^+$ reduction initiates at potential required to reduce the bimetallic site from Co$_{III}^{II}$ to Co$_{II}^{I}$. Based on the prevailing reaction pathways reported in the literature for other cobalt-based electrocatalysts, we postulate that catalytic H$^+$ reduction in Co$_2$L$^2$+ and Co$_2$LAc$^+$ is initiated by the formation of [Co$_{III}^{II}$–H] intermediates from Co$_{II}^{I}$ and H$_2$.28,42,20,67,78 Due to the close proximity of the two Co ions in Co$_2$L$^2$+ and Co$_2$LAc$^+$ (3.2 Å), the catalytic mechanism may also involve bimetallic intermediates in the form of adjacent [Co$_{III}^{III}$–H$_2$], or heterolytic attack of H$^+$ on [Co$_{III}^{III}$H$_2$]. Furthermore, the strong chelating nature of the N$_2$O$_2$ ligand may assist in the stability of the complex at low pH and low metal oxidation states. We are currently working toward full identification of the intermediate states and determination of a mechanistic cycle, as well as developing synthetic modifications to the ligand framework to shift the Co$_{II}^{II}$/Co$_{II}^{I}$ reduction to more positive potentials.

**EXPERIMENTAL SECTION**

**General Methods.** MALDI-TOF MS were obtained on a Bruker Ultraflex III. LR and HR ESI MS were obtained on a Thermo Electron Finnigan TSQ Quantum Ultra. Elemental analyses were obtained from Atlantic Microlabs, Inc., Norcross, GA. Electronic absorption spectra were obtained using a PerkinElmer Lambda 950 or Agilent 8453A spectrophotometer with a 1.0 cm quartz cell under a nitrogen atmosphere. Infrared absorption spectra were acquired using a Biorad Excalibur FTS-3000MX equipped with a liquid N$_2$-cooled MCT detector.

**Materials.** 4-tert-Butyl-2,6-diformylphenol was purchased from Sigma-Aldrich and was purified by column chromatography on silica gel with methylene chloride. All other chemicals and solvents used were of the highest purity available from commercial suppliers. MeCN was dried by circulating the N$_2$-purged solvent through a solid-state column purification system (Vacuum Atmospheres Company, Hawthorne, CA) prior to use.\textsuperscript{79} Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was purchased from Acros and twice recrystallized from hot ethanol before use in electrochemical experiments. [Zn$_2$LAc$^+$](ClO$_4$)$^-$ and [H$_2$L$^2$+](ClO$_4$)$^-$ were available from a previous study.\textsuperscript{30} Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of these compounds should be prepared and handled behind suitable protective shield.

[Co$_2$L](ClO$_4$)$^-$, Co(ClO$_4$)$_2$·6H$_2$O (200 mg, 0.55 mmol) and 4-tert-butyl-2,6-diformylphenol (100 mg, 0.48 mmol) were dissolved in 1 mL of methanol dropwise while stirring. The mixture was refluxed for 4 h under N$_2$, then cooled, and the volume of the solvent reduced under vacuum to approximately 2–3 mL. The resulting solution was kept at 0 °C for 24 h, yielding a brown powder, which was filtered and...
washed with cold methanol, followed by anhydrous diethyl ether. Successive recrystallizations from dichloromethane with diethyl ether gave \([\text{Co} \text{L}](\text{ClO}_4)_2\) (mass 189 mg, 78% yield). MALDI LR-MS (m/z): 789.18 [M – ClO\(_4\)]\(^{-}\). ESI LR-MS (m/z): 735.25 [M – 2(ClO\(_4\))] + (HCOO)\(^{-}\)]\(^{1+}\). Anal. Calcd for \([\text{M} + \text{H}]^+\): 344.62 [2(M + H)]\(^{1+}\). ESI HR-MS: Calcld for [M – 2(ClO\(_4\))] + (HCOO)\(^{-}\)]\(^{1+}\) 735.2474, found 735.2487. Anal. Calcld for C\(_{34}\)H\(_{48}\)N\(_6\)O\(_{10}\)Co\(_2\)Cl\(_2\)(H\(_2\)O)\(_3\): C, 43.27; H, 5.76; N, 8.90. Found: C, 43.73; H, 5.51; N, 8.29.

**ASSOCIATED CONTENT**

**Supporting Information**

Scheme depicting synthesis of \([\text{Co} \text{L}](\text{ClO}_4)_2\) and \([\text{Co} \text{L} \text{Ac}](\text{ClO}_4)_2\). Figures depicting FTIR and \(^1\)H NMR spectra and electrochemical results. Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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