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Rapid Water Reduction to H_2 Catalyzed by a Cobalt Bis(iminopyridine) Complex

Bryan D. Stubbert, Jonas C. Peters,* and Harry B. Gray*

Department of Chemistry, California Institute of Technology, Pasadena, California 91125, United States

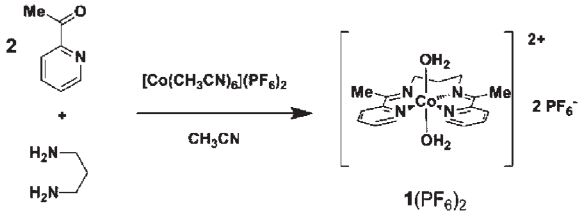
Supporting Information

ABSTRACT: A cobalt bis(iminopyridine) complex is a highly active electrocatalyst for water reduction, with an estimated apparent second order rate constant $k_{app} \leq 10^7$ $M^{-1}s^{-1}$ over a range of buffer/salt concentrations. Scan rate dependence data are consistent with freely diffusing electroactive species over pH 4−9 at room temperature for each of two catalytic reduction events, one of which is believed to be ligand based. Faradaic H_2 yields up to 87 ± 10% measured in constant potential electrolyses (−1.4 V vs SCE) confirm high reactivity and high fidelity in a catalyst supported by the noninnocent bis(iminopyridine) ligand. A mechanism involving initial reduction of Co^{2+} and subsequent protonation is proposed.

Ever-growing concern over the dangers of global climate change have sparked considerable interest in carbon-free and carbon-neutral energy sources.[1,2] Solar-driven water splitting to generate H_2 for use as a fuel and feedstock for a myriad of chemical processes,[2,3] including production of liquid fuels,[1,4] is among the most promising clean-energy strategies. Toward this end, scores of molecular catalysts for electrochemical[5] and photochemical[6] acid reduction have been reported. Molecular cobalt complexes[7] have been explored in the context of electrocatalytic H_2 evolution as mechanistic models and functional catalysts, ultimately for use in combination with light-absorbing materials in photoelectrochemical water-splitting devices.[4,8] While great strides have been made to better understand these systems in nonaqueous media, investigations of homogeneous and heterogeneous molecular catalysts in purely aqueous media—perhaps more relevant to scalable applications of photoelectrochemical water splitting—are lacking.[7,9]

A recent report from Chang and co-workers[10] described a rare example of a stable, highly active molecular cobalt electrocatalyst that reduces water to H_2 at neutral pH in aqueous buffer, reporting maximum current densities exceeding 4 mA/cm^2 at −1.8 V vs SCE.[11] In an effort to build on efficient nonaqueous proton reduction catalyzed by cobalt diimine and tetraimine complexes,[7] we have pursued a new type of cobalt bis(iminopyridine) catalyst displaying a high degree of steric and electronic tunability, possibly with ligand-centered redox activity for enhanced catalytic H_2 evolution from water.[12,13] Herein, we report a molecular cobalt electrocatalyst that rapidly reduces water to H_2 with current densities >20 mA/cm^2 attainable at a pH-independent operating potential of −1.3 V vs SCE.

Scheme 1. Synthesis of 1(PF_6)$_2$



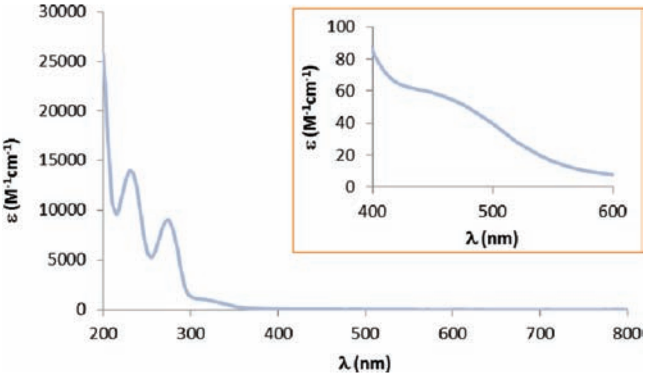


Figure 1. UV−visible absorbance spectrum of 1^{2+} (0.1−5 mM) in neutral H_2O (sealed quartz cells, 0.1−7.5 cm path length). (Inset) Enlarged view of absorbance centered at 450 nm.

The cobalt bis(iminopyridine) complex 1(PF_6)$_2$ was prepared via condensation of 1,3-diaminopropane with two equivalents of 2-acetylpyridine, templated by [$Co(CH_3CN)_6$](PF_6)$_2$ in acetonitrile at room temperature (Scheme 1). The red-orange residue obtained after drying in vacuo was converted to a powder by grinding the residue in a suspension of Et_2O, affording 1(PF_6)$_2$ as an orange solid in 93% yield. The electronic absorbance spectrum of 1^{2+} in water (Figure 1) shows two intense ligand $\pi \rightarrow \pi^*$ peaks at 230 and 275 nm (ε = 14 000 and 9500 M^{-1} cm^{-1}, respectively), and a weak feature (ε = 60 M^{-1} cm^{-1}) at 450 nm assigned to a Co^{2+} *d-d* transition (inset, Figure 1). An additional band at 310 nm was observed with ε = 940 M^{-1} cm^{-1}. Each λ_{max} obeys Beer's law over the concentration range 0.1 to 5 mM, showing no significant aggregation of Co^{2+} in aqueous solution at concentrations relevant to catalysis.

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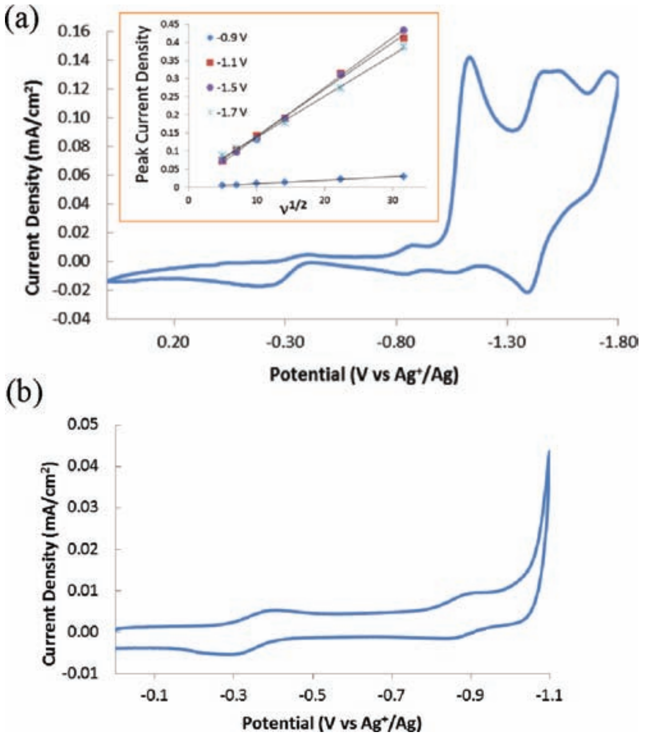


Figure 2. (a) Representative cyclic voltammogram of 0.5 mM $\mathbf{1}^{2+}$ in CH_3CN solution (0.1 M TBAH, 100 mV/s, GCE area = 0.07 cm^2). (Inset) Plot of current density vs (scan rate)$^{1/2}$ for reductions relevant to electrocatalysis (units: mA/cm^2 vs $(mV/s)^{1/2}$). Fc^+/Fc observed at +0.14 V vs Ag^+/Ag (see Supporting Information for full details). (b) Reductions assigned as cobalt centered (50 mV/s).

In acetonitrile electrolyte, there are two reductions assigned to the $Co^{3+/2+}$ (quasireversible) and $Co^{2+/1+}$ (reversible) couples at −0.34 V and −0.86 V (vs Ag^+/Ag, Figure 2). Interestingly, additional reductions are evident with j_{max} at −1.15, −1.48, and −1.73 V. The magnitude of current drawn in the reduction at −1.15 V is consistent with reduction of residual water of coordination from $\mathbf{1}^{2+}$ in conjunction with a ligand reduction. Scan rate analyses of voltammograms obtained under anaerobic, anhydrous conditions exhibit linear dependences in plots of j_{max} vs $\nu^{1/2}$ (inset, Figure 2a), as expected for diffusional species[14] at all observed redox events. In buffered aqueous media from pH 1−9, the $Co^{3+/2+}$ reduction potential measured at a static mercury drop electrode is irreversible and pH dependent with a slope of −73 mV per decade. From the Pourbaix plot in Figure 3, a thermodynamic (pH 0) value of −0.38 V vs SCE was estimated for the irreversible peak current, quite similar to the $Co^{3+/2+}$ couple obtained in CH_3CN. At pH ≤ 3, partial complex decomposition was observed upon further reduction, as evidenced by retention of the wave assigned to the pH dependent $Co^{3+/2+}$ couple and marked decrease in the current density expected for water reduction. No significant dependence on buffer concentration (5−500 mM) or salinity (up to 3.5%) was observed.

Electrochemical data obtained in aqueous anaerobic media display irreversible reduction waves at potentials near the presumed $Co^{2+/1+}$ redox couple and the first ligand reduction, consistent with electrocatalytic water reduction (Figure 4). Indeed, Faradaic efficiencies measured volumetrically (>90%) and by gas chromatography (up to 87 ± 10%) confirm the presence of H_2 and the absence of significant catalyst decomposition. Controlled potential bulk electrolyses performed at each of two operating potentials (−1.0 and −1.4 V vs SCE) for 1 h in pH 2, 5, and 8 solutions containing 0.1 M buffer (phosphate or citrate) and 0.5 mM concentration of $\mathbf{1}^{2+}$, confirm H_2 evolution.[15] At pH 8, a modest Faradaic efficiency of 60 ± 10% was obtained, corresponding to 10 L H_2 (mol cat)$^{-1}$ h^{-1}(cm^2 Hg)$^{-1}$. Regardless of pH, H_2 yields drop significantly at operating potentials < −1.5 V vs SCE, owing to catalyst decomposition at more reducing potentials, possibly through reactivity of a ligand centered radical (eq 1).[16,17]

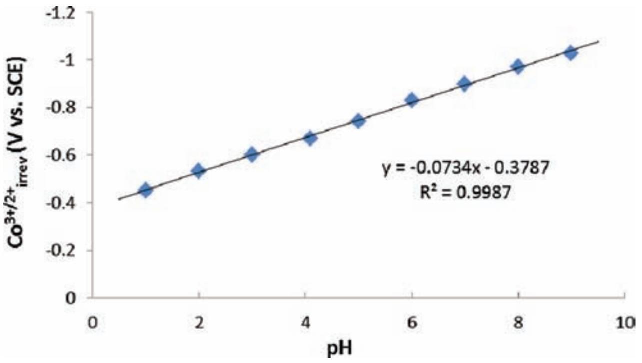
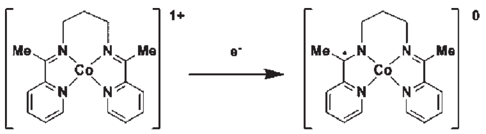


Figure 3. Pourbaix plot for irreversible reduction assigned to $\mathbf{1}^{3+/2+}$ in aqueous buffer (pH 1, 0.1 M KCl/HCl; pH 2, 7, 8, 0.05 M P_i; pH 3−6, 0.05 M citrate; pH 9, 0.05 M borax). Static Hg drop electrode (0.013 cm^2), 100 mV/s.



(1)

Faradaic H_2 yields of 75 and 87 ± 10% were obtained for pH 2 and 5 solutions, corresponding to 10^2 and 5 × 10 L H_2 (mol cat)$^{-1}$ h^{-1}(cm^2 Hg)$^{-1}$, respectively, suggesting that an optimal performance range may be operative at moderate pH. Moreover, these efficiencies confirm that CV data may be used to estimate catalytic efficiency for waves observed at potentials less negative than −1.4 V vs SCE. It is also noteworthy that the volume of H_2 evolved at −1.0 V, near the $Co^{2+/1+}$ reduction wave of $\mathbf{1}^{2+}$, was much less than at −1.4 V, regardless of pH. While multiple H_2 evolving processes (vide infra) and the relative overpotential/driving force would have an additive effect on H_2 yield,[14] CV data indicated much higher j_{max} at potentials close to the second (catalytic) reduction. On the basis of literature precedent, this increase in catalyst activity is tentatively ascribed to a ligand centered reduction of the putative $[Co^{3+}{-}H]$ intermediate.[18,19]

From these analyses, we postulate that water reduction proceeds through slightly different pathways according to pH (eqs 2−6), generally beginning with reduction of cobalt in $\mathbf{1}^{2+}$ (eq 2) and terminating with H_2 evolution via binuclear recombination and/or direct protonation of a putative $[Co{-}H]^{n+}$ intermediate.[20]

$$[Co^{2+}(L_4)]^{2+} + e^- \rightarrow [Co^{1+}(L_4)]^{1+} \qquad (2)$$

$$[Co^{1+}(L_4)]^{1+} + H_3O^+ \rightarrow [Co^{3+}{-}H(L_4)]^{2+} + H_2O \qquad (3)$$

$$[Co^{1+}(L_4)]^{1+} + e^- \rightarrow [Co^{1+}(L_4{}^{\cdot -})]^0 \qquad (4)$$

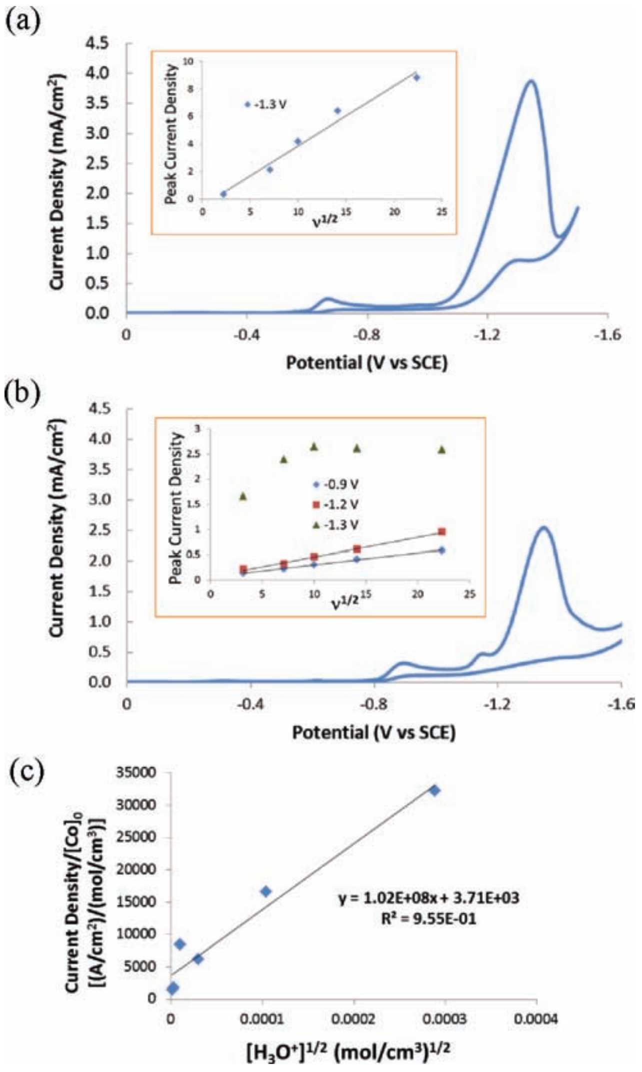


Figure 4. Representative cyclic voltammograms of $\mathbf{1}^{2+}$ in 0.05 M aqueous buffer solutions (Hg drop electrode area = 0.013 cm^2). (a) $\mathbf{1}^{2+}$ (0.1 mM) in pH 4.1 citrate buffer. (b) $\mathbf{1}^{2+}$ (0.3 mM) in pH 7.0 phosphate buffer. (Insets) Plots of current density vs (scan rate)$^{1/2}$ for reductions relevant to electrocatalysis (units: mA/cm^2 vs (mV/s)$^{1/2}$). (c) Plot of $j_{max}/[\mathbf{1}^{2+}]_0$ vs $[\mathrm{H_3O^+}]^{1/2}$ in pH 4−9 aqueous 0.05 M buffer solutions (see Supporting Information for full details).

$$[\mathrm{Co}^{1+}(\mathrm{L_4}^{\bullet -})]^0 + \mathrm{H_3O^+} \rightarrow [\mathrm{Co}^{3+}\text{−}\mathrm{H}(\mathrm{L_4}^{\bullet -})]^{1+} \tag{5a}$$

$$[\mathrm{Co}^{1+}(\mathrm{L_4}^{\bullet -})]^0 + \mathrm{H_3O^+} \rightarrow [\mathrm{Co}^{2+}\text{−}\mathrm{H}(\mathrm{L_4})]^{1+} \tag{5b}$$

$$[\mathrm{Co}^{3+} - \mathrm{H}(\mathrm{L_4})]^{2+} + e^- \rightarrow [\mathrm{Co}^{3+}\text{−}\mathrm{H}(\mathrm{L_4}^{\bullet -})]^{1+} \tag{6a}$$

$$[\mathrm{Co}^{3+} - \mathrm{H}(\mathrm{L_4})]^{2+} + e^- \rightarrow [\mathrm{Co}^{2+}\text{−}\mathrm{H}(\mathrm{L_4})]^{1+} \tag{6b}$$

At pH ≥ 7, where the $\mathrm{Co}^{2+/1+}$ reduction is distinct from the large catalytic wave (Figure 4b), protonation of Co^{1+} is not the primary route to $\mathrm{H_2}$ evolution and is slow on the time scale of the CV experiment, though electrolyses at −1.0 V vs SCE indicate minimal $\mathrm{H_2}$ production. Thus, at low $[\mathrm{H_3O^+}]$, we favor protonation of a presumed doubly reduced complex,[7,9c,9d,10,21,22] leading to either $[\mathrm{Co}^{3+}\text{−}\mathrm{H}(\mathrm{L_4}^{\bullet -})]^{1+}$ or $[\mathrm{Co}^{2+}\text{−}\mathrm{H}(\mathrm{L_4})]^{1+}$ (eqs 4−5) as the primary route to water reduction. At pH ≤ 6, where the reduction wave assigned to the $\mathrm{Co}^{2+/1+}$ couple is *not* well resolved from the large catalytic wave, it is likely that significant water reduction occurs via protonation at Co^{1+} (eq 3), as is typically proposed in the turnover limiting step for cobalt electrocatalysts in nonaqueous media.[7,9,19,23] Additionally, we speculate that a "reduced-ligand" pathway (eqs 5, 6) may also be operative at high $[\mathrm{H_3O^+}]$, where $\mathrm{H_2}$ evolution is presumably faster than ligand decomposition. Although the relative contributions are indistinguishable in this analysis, we suspect that these processes are complementary $\mathrm{H_2}$ evolution pathways.

For freely diffusing catalyst and substrate (neither species adsorbed or covalently attached to the working electrode), an estimate of the apparent (turnover limiting) rate of protonation of a reduced cobalt species (k_{app}) can be made from the following expression

$$j = nFC_p^\circ(Dk_{app}C_s^\circ)^{1/2} \tag{7}$$

where $n = 2$ is the stoichiometric factor for the number of electrons in the catalyzed reaction, F is the Faraday constant, C_p° and C_s° are the concentrations of catalyst and substrate (mol/cm^3), respectively, j is the maximum plateau current density (A/cm^2), and D is the catalyst diffusion coefficient (4×10^{-5} cm^2/s).[24] A plot of maximum current density as a function of pH ($j_{max}/[\mathbf{1}^{2+}]_0$ vs $[\mathrm{H_3O^+}]^{1/2}$) shows the linear dependence expected for protonation of a reduced cobalt species (Figure 4c). Over the range of conditions studied at both mercury (aqueous media) and glassy carbon ($\mathrm{CH_3CN}$ media) working electrodes, maximum current densities in cyclic and linear sweep voltammograms of $\mathbf{1}^{2+}$ display a linear dependence on $\nu^{1/2}$, typical of diffusional species without significant electrode adsorption (inset, Figures 2 and 4).[14] Interestingly, the scan rate dependence for the primary catalytic reduction at −1.3 V disappears at pH 7, which offers no information regarding the extent of electrode adsorption but does indicate steady state behavior.[14] A linear dependence of j_{max} on [Co] also was observed at ≤1 mM (Figure S3, Supporting Information), with a shift to slightly more negative potentials and a sharp flattening of j_{max} at higher catalyst concentrations, reminiscent of saturation kinetics.[25] Note that in the absence of an extended plateau region for j_{max}, eq 2 provides only an approximation of k_{app} in the present system (calculated for j_{max} measured at 100 mV/s).[26] From the slope of the linear fit in Figure 4c, a value of $k_{app} = 7 \times 10^6$ M^{-1} s^{-1} was obtained, roughly on par with $\mathrm{H_2}$ production rates determined from controlled potential electrolyses. Similar complexes thought to exhibit turnover limiting protonation of reduced cobalt species frequently[7,9,23] display $k_{app} \leq 10^5$ M^{-1} s^{-1} in electrochemical experiments. While a stark difference in reactivity is apparent from observed current densities, the complexities in assigning a precise electrocatalytic mechanism involving at least partial ligand reduction raises questions regarding the validity and relevance of $k_{app} \leq 10^7$ M^{-1}s^{-1} obtained via this treatment. Additionally, photochemical experiments aimed at better estimating the rate of protonation of reduced cobalt species and to more rigorously establish the extent of homogeneity in solution are underway.

In summary, we have discovered a highly active electrocatalyst for water reduction in buffered aqueous media. The incorporation of a redox noninnocent bis(iminopyridine) ligand for cobalt presumably results in enhanced electrocatalysis without significant ligand decomposition at moderate pH, owing to facile reduction of $[\mathrm{Co{-}H}]^{n+}$ species. The high current densities measured for $\mathbf{1}^{2+}$ at moderate $[H_3O^+]$ compare favorably with analogous values for acid reduction catalyzed by cobalt complexes in nonaqueous media, albeit operating at a significant overpotential. Moreover, the apparent diffusional nature of **1** should permit more detailed mechanistic study of molecular catalysis of water reduction. Ongoing studies aim to lower the minimal overpotential required for H_2 evolution in aqueous media via ligand modification.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Full citation for reference 2, and experimental details of synthesis, characterization, and electrochemical experiments, including representative voltammograms, enlarged scan rate dependence plots, and Table S1 summarizing the relevant potentials in Figures 2 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

hbgray@caltech.edu; jpeters@caltech.edu

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(26) The increase in j_{max} with increasing scan rate suggests that diffusion limited plateau current densities would be larger than at 100 mV/s, which would result in a larger calculated k_{app} (as seen at pH 7; inset Figure 4b and Figure S2, Supporting Information).