

Computational Study of Anomalous Reduction Potentials for Hydrogen Evolution Catalyzed by Cobalt Dithiolene Complexes

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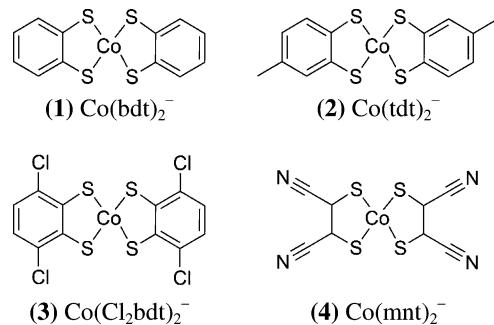
 Supporting Information

ABSTRACT: The design of efficient hydrogen-evolving catalysts based on earth-abundant materials is important for developing alternative renewable energy sources. A series of four hydrogen-evolving cobalt dithiolene complexes in acetonitrile–water solvent is studied with computational methods. $\text{Co}(\text{mnt})_2$ (mnt = maleonitrile-2,3-dithiolate) has been shown experimentally to be the least active electrocatalyst (i.e., to produce H_2 at the most negative potential) in this series, even though it has the most strongly electron-withdrawing substituents and the least negative $\text{Co}^{\text{III}/\text{II}}$ reduction potential. The calculations provide an explanation for this anomalous behavior in terms of protonation of the sulfur atoms on the dithiolene ligands after the initial $\text{Co}^{\text{III}/\text{II}}$ reduction. One fewer sulfur atom is protonated in the $\text{Co}^{\text{II}}(\text{mnt})_2$ complex than in the other three complexes in the series. As a result, the subsequent $\text{Co}^{\text{II}/\text{I}}$ reduction step occurs at the most negative potential for $\text{Co}(\text{mnt})_2$. According to the proposed mechanism, the resulting Co^{I} complex undergoes intramolecular proton transfer to form a catalytically active Co^{III} -hydride that can further react to produce H_2 . Understanding the impact of ligand protonation on electrocatalytic activity is important for designing more effective electrocatalysts for solar devices.

Direct solar-to-fuel energy conversion processes with earth-abundant materials are of great importance for meeting global energy demands. Many proposed water-splitting devices require hydrogen-evolving catalysts that can perform efficiently in aqueous conditions. Cobaloxime catalysts have been shown to evolve hydrogen electrochemically at relatively low overpotentials^{1,2} and photochemically with reasonable activity.³ Most experiments with these catalysts were performed in nonaqueous solvents,⁴ prompting more recent studies in aqueous media.⁵ Computational methods have also been employed to characterize the physical properties and mechanisms of cobaloxime electrocatalysts.^{6–9}

Recently, a series of cobalt dithiolene complexes [$\text{Co}(\text{bdt})_2$ (bdt = benzene-1,2-dithiolate) (1), $\text{Co}(\text{tdt})_2$ (tdt = toluene-3,4-dithiolate) (2), $\text{Co}(\text{Cl}_2\text{bdt})_2$ (Cl_2bdt = 3,6-dichloro-bdt) (3), and $\text{Co}(\text{mnt})_2$ (mnt = maleonitrile-2,3-dithiolate) (4)], depicted in Chart 1, has been shown to evolve hydrogen in 1:1 (v:v) $\text{CH}_3\text{CN}:\text{H}_2\text{O}$.^{10,11} The reduction potentials of the $[\text{CoL}_2]^-/[\text{CoL}_2]^{2-}$ couple (i.e., the $\text{Co}^{\text{III}/\text{II}}$ reduction potentials) for these catalysts are ordered according to the electron-

Chart 1. Cobalt Dithiolene Complexes



withdrawing character of the dithiolene substituents: 4 > 3 > 1 > 2, where complex 4 exhibits the least negative reduction potential. Moreover, based on the turnover frequencies measured photochemically, the photocatalytic activity of these complexes follows the same order, where complex 4 is the most active photocatalyst. In contrast, the electrocatalytic data obtained upon addition of trifluoroacetic acid indicate a different ordering of the reduction potentials associated with the catalytic wave: 3 > 1 > 2 > 4, where complex 4 operates at the most negative potential. Since electrocatalytic activity is typically measured by the operating overpotential, these results show that complex 4 is the least active electrocatalyst. Thus, complex 4 produces hydrogen at the most negative potential, even though its $\text{Co}^{\text{III}/\text{II}}$ reduction potential is the least negative.

In this Communication, we investigate this series of cobalt dithiolene complexes computationally to provide an explanation for the anomalous behavior of complex 4. Previous studies indicated that cobalt dithiolene complexes have mixed metal–ligand character frontier orbitals,^{12,13} suggesting that protonation could occur at the ligands as well as the cobalt center.¹¹ We examine the possibility of both ligand and metal protonation along the reaction pathways for hydrogen evolution by calculating the reduction potentials and relative pK_a 's for the various species. Our calculations suggest that ligand protonation at one or two sulfur atoms may occur directly after the initial electrochemical reduction. Due to differences in the strengths of the electron-withdrawing groups on the dithiolene ligands, one more sulfur atom is protonated in complexes 1–3 than in complex 4. As a result, the subsequent reduction step occurs at a more negative potential

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Table 1. Calculated Reduction Potentials for Complexes 1–4^a

	$E^\circ[\text{Co}^{\text{III}/\text{II}}]$		$E^\circ[\text{Co}^{\text{II}/\text{I}}]$		$E^\circ[\text{Co}^{\text{II}/\text{I}}\text{-}(\text{SH})_2]$		$E^\circ[\text{Co}^{\text{II}/\text{I}}\text{-}(\text{SH})]$	
	calc	expt ^b	calc	expt ^b	calc	expt ^c	calc	expt ^c
1	−0.64 ^d	−0.64	−2.74		−1.21 ^e	(−1.21)	−1.89	
2	−0.70	−0.70	−2.83		−1.24	(−1.32)	−1.96	
3	−0.52	−0.51	−2.51		−1.03	(−0.95)	−1.66	
4	N/A ^f	−0.04	−1.43	−1.49	−0.35		−1.13	(−1.37)

^aValues given in volts vs SCE in 1:1 (v:v) $\text{CH}_3\text{CN}:\text{H}_2\text{O}$. ^bExperimental $E_{1/2}$ from ref 11. ^cExperimental i_{pc} from ref 11. Values in parentheses indicate that we have assigned i_{pc} to reduction potentials at different protonation states. ^d $E^\circ[\text{Co}^{\text{III}/\text{II}}\text{-}(\text{bdt})_2]$ was used as the reference in the isodesmic reactions, so this value agrees by construction, and all other reduction potentials without protonation are calculated relative to this value. ^e $E^\circ[\text{Co}^{\text{II}/\text{I}}\text{-}(\text{bdt})_2\text{-}(\text{SH})_2]$ was used as the reference in the isodesmic reactions, so this value agrees by construction, and all other reduction potentials with protonation are calculated relative to this value. ^f $\text{Co}^{\text{III}}(\text{mnt})_2^-$ exists as a dimer, so this value was not calculated.

for complex 4 than for complexes 1–3. According to this analysis, complex 4 is the least active electrocatalyst because of a lower degree of ligand protonation.

We calculated the reduction potentials and relative pK_a 's with density functional theory (DFT). The reaction free energy for reduction or deprotonation of a molecule in solution was calculated at $T = 298.15$ K including contributions from zero-point energy and entropy. We used isodesmic reactions to eliminate systematic computational errors in the DFT calculations due to limitations in the basis set and exchange-correlation functional. In this approach, the reduction potentials and pK_a 's are calculated relative to a specified reference reaction, thereby eliminating the need to calculate the free energy of a proton in solution.^{6,7}

For each complex, we performed geometry optimizations for all possible protonation sites and spin states and calculated the reduction potentials and pK_a 's for the states with the lowest free energy. The structures were optimized with DFT using Gaussian 09 at the B3P86/6-311+G(d,p) level of theory in solution.^{14a} Additional calculations with the 6-311+G(2d,p) basis set are provided in Supporting Information (SI) and lead to virtually identical results. Solvent effects were described with the conductor-like polarizable continuum model^{14b,c} (C-PCM) including non-electrostatic interactions resulting from dispersion, repulsion, and cavity formation. Experiments were carried out in a 1:1 (v:v) $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ solution, which has an experimental dielectric constant of $\epsilon_0 \approx 50$.¹⁵ We used an average of $1/\epsilon$ for acetonitrile and water to give $\epsilon_0 = 49$ and $\epsilon_\infty = 1.79$. Although the C-PCM method was not designed to treat mixed solvents, the qualitative trends are the same in pure water, pure acetonitrile, and mixed solvent, as indicated in SI.

The monoanion cobalt dithiolenes are planar and correspond to triplet states, as shown by X-ray absorption spectroscopy.^{11,16} Complex 4 is known to form a dimer in solution but has been shown to exist primarily as a monomer after initial reduction to the dianion.^{11,17} Our DFT calculations of relative free energies are consistent with experiment in that the triplet monoanion is the thermodynamically favored spin state for all four complexes. The primary formal oxidation state of the cobalt center in the monoanion is Co^{III} , although some Co^{II} character is present due to resonance forms.^{16,17} The optimized Co–S and S–C bond lengths agree with the crystal structures^{10,11} for the triplet monoanions within 0.03 Å, as shown in SI. The doublet and quartet states of the dianion, formally Co^{II} , are nearly degenerate. While there is evidence that Co^{II} exists as a doublet in the gas phase,¹² solvation could cause the quartet state to predominate.¹⁸ Given this importance of solvation effects, all geometry optimizations were performed in solvent. The doublet Co^{II} species remained planar upon

optimization, while the quartet Co^{II} adopted a tetrahedral geometry. The quartet Co^{II} was calculated to have the lowest free energy in solution for all four complexes. The thermodynamically favored Co^{I} species was found to be a tetrahedral triplet, while the thermodynamically favored Co^{III} -hydride species was found to be a square pyramidal singlet. Note that a water or acetonitrile ligand could occupy the sixth octahedral site in singlet Co^{III} -hydride. The calculated pK_a 's for complex 1 with these axial ligands are provided in SI and indicate a relatively small effect.

The calculated reduction potentials and corresponding experimental values are given in Table 1. Cyclic voltammetry experiments showed that in the absence of acid, the initial $\text{Co}^{\text{III}/\text{II}}$ reduction potentials range from −0.04 to −0.70 V vs SCE with the ordering 4 > 3 > 1 > 2.¹¹ A second peak was observed for complex 4, corresponding to the $\text{Co}^{\text{II}/\text{I}}$ couple. The other complexes did not exhibit a second peak before irreversible reduction of solvent/electrolyte. Table 1 illustrates that the calculated values are in excellent agreement with the corresponding experimental values. Note that the ordering of these reduction potentials is correlated with the strength of the electron-withdrawing substituents on the dithiolene ligands.

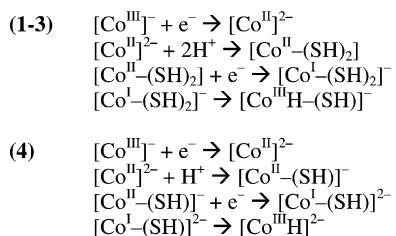
Cyclic voltammetry experiments indicate that the reduction potential of the catalytic wave is more negative for complex 4 than for complexes 1–3, with an ordering of 3 > 1 > 2 > 4. This ordering is not consistent with the ordering of the $\text{Co}^{\text{III}/\text{II}}$ reduction potentials in the absence of acid or the degree of electron-withdrawing character of the substituents. Specifically, complex 4 has the least negative $\text{Co}^{\text{III}/\text{II}}$ reduction potential but the most negative reduction potential associated with the catalytic wave. Our calculations provide an explanation for this discrepancy in terms of protonation of the sulfur atoms on the dithiolene ligands. The calculations indicate that more highly protonated complexes are more easily reduced, as expected because of the additional positive charge associated with the protons. This trend suggests that complex 4 is less protonated than complexes 1–3 for the reduction step associated with the catalytic wave. Moreover, cyclic voltammograms obtained over a range of acidities (Figure S4 in ref 11) indicate that complex 4 is likely protonated to some extent after the initial reduction to the Co^{II} dianion because the reduction potential of the catalytic wave is less negative than the $\text{Co}^{\text{II}/\text{I}}$ reduction potential in the absence of acid and plateaus at higher acid concentrations.¹¹

Based on this analysis, we tentatively assign the catalytic wave in cyclic voltammetry to the $\text{Co}^{\text{II}/\text{I}}$ couple of the doubly protonated species for complexes 1–3 and the singly protonated species for complex 4. A comparison between the calculated and experimental reduction potentials based on these assignments is given in Table 1. For complex 4, the calculated

$E^\circ[\text{Co}^{\text{II}/\text{I}}\text{-(SH)}]$, where (SH) denotes a protonated sulfur atom, is in much better agreement with the experimental reduction potential of the catalytic wave than is the calculated $E^\circ[\text{Co}^{\text{II}/\text{I}}\text{-(SH)}_2]$, providing support for the assumption that only one sulfur atom is protonated in complex 4. The overall agreement between the calculated and experimental values in Table 1 provides further support for our assignments, although it is possible that other assignments consistent with the data could be found. The somewhat larger error for complex 4 is probably due to the different nature of its maleonitrile substituents compared to the benzene-substituted reference system, as well as the difference in degree of protonation.

Scheme 1 presents our proposed mechanisms for the generation of a Co^{III} -hydride. These mechanisms are consistent

Scheme 1. Proposed Mechanism for Co^{III} -Hydride Generation



with the calculated reduction potentials given in Table 1 and the calculated relative $\text{p}K_a$'s given in Figure 1. Qualitatively, a higher $\text{p}K_a$ corresponds to thermodynamically more favorable protonation. The relative $\text{p}K_a$'s for each complex are expected to be reliable, but comparisons between complexes may not be quantitatively accurate, particularly for complex 4 due to the different nature of its substituents. For this mechanism, the $\text{p}K_a$ of trifluoroacetic acid, which was used in the experiments, is presumed to be within a few $\text{p}K_a$ units of zero in Figure 1 based on experimental data,^{10,11} although the computational methods do not allow a quantitatively accurate comparison between the $\text{p}K_a$'s of the acid and cobalt complexes.

Cyclic voltammetry experiments showed that the peak corresponding to the $\text{Co}^{\text{III}/\text{II}}$ couple is unaffected upon addition of acid for complex 1,¹⁰ suggesting that Co^{III} is unlikely to be protonated. The calculations are consistent with this experimental observation that the calculated relative $\text{p}K_a$ for protonation of a ligand in Co^{III} (black lines in Figure 1) is lower than the other values provided for each complex.¹⁹ Thus, we assume that the first step in the mechanism of all four complexes is the reduction of the monoanionic Co^{III} species to the dianionic Co^{II} species.

After this initial reduction, either one or two sulfur atoms in the dithiolene ligands are protonated in the proposed mechanisms. For complexes 1–3, the dithiolene ligands can be doubly protonated (i.e., two sulfur atoms can be protonated), as shown by the relatively high $\text{p}K_a$ values of both blue lines in Figure 1. For complex 4, the protonation of the second sulfur atom on the dithiolene ligands is less thermodynamically favorable (lower blue line for complex 4 in Figure 1) and therefore is unlikely to occur. Another possibility is that the cobalt center of Co^{II} is protonated, leading to a Co^{IV} -hydride (purple lines). Note that protonation of the cobalt (purple lines) is less thermodynamically favorable than protonation of a sulfur on the dithiolene ligands (blue lines) for all four complexes in the Co^{II} state. Further justification of

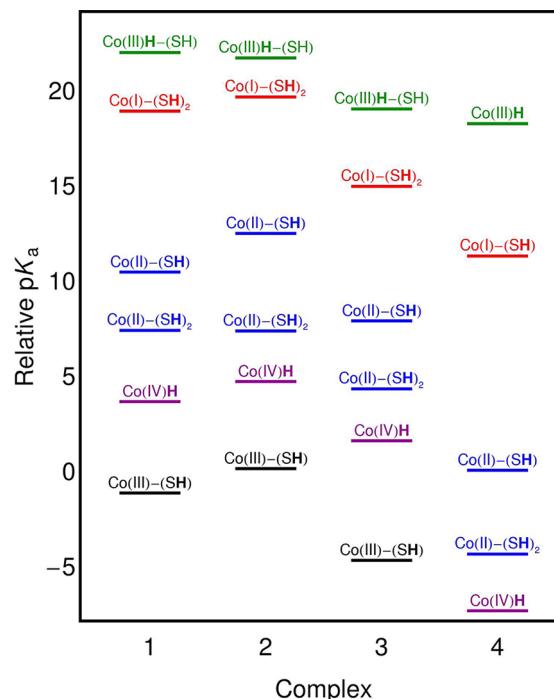


Figure 1. Calculated $\text{p}K_a$'s of all four complexes relative to the $\text{p}K_a$ of $\text{Co}^{\text{III}}(\text{tdt})_2\text{-(SH)}$. The bold H is the proton removed to calculate the $\text{p}K_a$, and only the protonated sulfurs are shown. The species in black correspond to protonation of the initial monoanion, Co^{III} , which is not expected to occur. Reduction to Co^{II} results in protonation of the dithiolene ligands, shown in blue, or the cobalt center, shown in purple. The latter is less likely due to the lower $\text{p}K_a$. According to the proposed mechanism, complexes 1–3 are doubly protonated, while complex 4 is only singly protonated at the dithiolene ligands due to the low $\text{p}K_a$ of $\text{Co}^{\text{II}}(\text{mnt})\text{-(SH)}_2$. After further reduction, Co^{I} , shown in red, undergoes intramolecular proton transfer to form Co^{III} -hydride, shown in green. Expanded version provided in SI.

ligand protonation is provided by an analysis of the frontier orbitals in SI.

Following the double protonation of the ligands for complexes 1–3 and the single protonation of a ligand in complex 4, the Co^{II} complex is reduced to Co^{I} . The calculated $\text{Co}^{\text{II}/\text{I}}$ reduction potentials for all four complexes are consistent with the experimentally measured values (Table 1). Protonation of the ligands facilitates the $\text{Co}^{\text{II}/\text{I}}$ reduction, as discussed above.

Subsequently, the Co^{I} complex (red lines in Figure 1) undergoes intramolecular proton transfer to form a Co^{III} -hydride (green lines). Based on the relative $\text{p}K_a$'s of these complexes, this intramolecular proton transfer step is thermodynamically favorable. Furthermore, the $\text{p}K_a$ difference between the Co^{III} -hydride and Co^{I} complexes increases with electron-withdrawing character of the dithiolene substituents. Larger $\text{p}K_a$ differences indicate more thermodynamically favorable intramolecular proton transfer, thereby providing one possible explanation for complex 4 exhibiting the largest photochemically measured turnover frequency, although free energy barriers have not been calculated.

Several alternative mechanisms are discussed in SI. For example, the Co^{I} center could be protonated intermolecularly from an acid rather than intramolecularly, or protonation of an additional sulfur atom could occur prior to the formation of the Co^{III} -hydride. The relative $\text{p}K_a$'s of these species and others are

provided in an expanded version of Figure 1 in SI. We also present an alternative scheme in which complexes **1–3** have a single protonated ligand and complex **4** has no protonated ligands for the $\text{Co}^{\text{II}/\text{I}}$ reduction step. Another possibility is that complexes **1–3** have doubly protonated ligands and complex **4** has no protonated ligands for the $\text{Co}^{\text{II}/\text{I}}$ reduction step. These alternative schemes may not be consistent with the experimental observation of a less negative $\text{Co}^{\text{II}/\text{I}}$ reduction potential for complex **4** in the presence of acid.¹¹ Other mechanisms involving concerted proton-coupled electron transfer are also possible.

The generation of H_2 typically requires a Co^{III} -hydride intermediate.^{2,6} The Co^{III} -hydride species could produce H_2 by reacting directly with acid to regenerate the Co^{III} species, by reduction to a Co^{II} -hydride species followed by reaction with an acid, or by a bimetallic mechanism involving two Co -hydride complexes. For complexes **1–3**, $\text{Co}^{\text{III}}\text{H}-(\text{SH})$ could produce H_2 from the hydride on the cobalt and the proton on the sulfur. Moreover, additional steps involving deprotonation and protonation of the ligands could lead to a multitude of alternative pathways toward H_2 production. The examination of these steps is beyond the scope of this study.

In this Communication, we used computational methods to investigate the electrochemical reaction pathway for hydrogen evolution catalyzed by cobalt dithiolene complexes with varying electron-withdrawing substituents. In conjunction with available experimental data, our calculations suggest that the reduction potential of the catalytic wave in cyclic voltammetry corresponds to $E^\circ[\text{Co}^{\text{II}/\text{I}}-(\text{SH})_2]$ for complexes **1–3** and $E^\circ[\text{Co}^{\text{II}/\text{I}}-(\text{SH})]$ for complex **4**. Complex **4** is less likely to have two protonated sulfur atoms because it has the most strongly electron-withdrawing substituents on the dithiolene ligands. Our proposed mechanism involves the following steps: initial $\text{Co}^{\text{III}/\text{II}}$ reduction, protonation of the dithiolene ligands in the Co^{II} species, $\text{Co}^{\text{II}/\text{I}}$ reduction of the ligand-protonated species, and intramolecular proton transfer within the Co^{I} species to form a Co^{III} -hydride. The overpotential required for hydrogen evolution is lower for complexes **1–3** than for complex **4** because of the positive charge associated with the second proton on the dithiolene ligands in complexes **1–3**. We also propose alternative mechanisms in which the reduction potential of the catalytic wave in cyclic voltammetry corresponds to $E^\circ[\text{Co}^{\text{II}/\text{I}}-(\text{SH})]$ for complexes **1–3** and $E^\circ[\text{Co}^{\text{II}/\text{I}}]$ for complex **4**. All of these mechanisms explain the experimental observation that complex **4** is the least active electrocatalyst in terms of a lower degree of ligand protonation. Understanding the impact of ligand protonation on electrocatalytic activity is important for designing more effective electrocatalysts for solar devices.

ASSOCIATED CONTENT

Supporting Information

Comparison of calculated bond lengths to crystal structures for triplet Co^{III} ; expanded version of Figure 1; analysis of frontier orbitals; relative $\text{p}K_a$'s with axial solvent ligands; reduction potentials calculated with Bondi radii, in CH_3CN , in H_2O , and with 6-311+G(2d,p) basis set; alternative proposed mechanisms; complete ref 14a; coordinates and energies of lowest free energy optimized structures. 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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