Canadian Journal of Chemistry
Revue canadienne de chimie

A Computational Investigation into Nickel-Bis(Diselenolene) Complexes as Potential Catalysts for Reduction of H^+ to H_2

Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2017-0565.R1
Manuscript Type:	Article
Date Submitted by the Author:	26-Oct-2017
Complete List of Authors:	Boychuk, Briana; Brandon University, Chemistry Bushnell, Eric; Brandon University, Chemistry
Is the invited manuscript for consideration in a Special Issue?:	N/A
Keyword:	Hydrogen Evolution Reaction, HER Catalysts, Alternative Fuels, Diselenolene, Density Functional Theory

SCHOLARONE™
Manuscripts

A Computational Investigation into Nickel-Bis(Diselenolene) Complexes as Potential Catalysts for Reduction of H^+ to H_2

*Briana T. A. Boychuk and Eric A. C. Bushnell**

Department of Chemistry, Brandon University, 270-18th Street, Brandon, Manitoba R7A 6A9, Canada

AUTHOR EMAIL ADDRESS: bushnelle@brandonu.ca

RECEIVED DATE: to be inserted after manuscript is accepted

TITLE RUNNING HEAD: A Computational Investigation into Nickel-Bis(Diselenolene) Complexes as Potential Catalysts for Reduction of H^+ to H_2

* Author to whom correspondence should be addressed. Email: bushnelle@brandonu.ca

Abstract

As a result of burning fossil fuels levels of greenhouse gases in our atmosphere are increasing at an alarming rate. Such an increase in greenhouse gases threatens our planet due to global climate change. To reduce the production of greenhouse gases we must switch from fossil fuels to alternative fuels for energy. The most viable alternative energy source involves the conversion of solar energy into chemical energy via the photocatalytic splitting of water to form molecular hydrogen. In the present work the Ni-bis(1,2-diamine-diselenolene) and Ni-bis(1,2-dicyano-diselenolene) complexes were studied using Density Functional Theory (DFT). From the results it was found that the 1,2-diamine-diselenolene and 1,2-dicyano-diselenolene nickel complexes catalyze the formation of $\text{H}_2(\text{g})$ with overall reaction Gibbs energies of $+8.7 \text{ kJ mol}^{-1}$ and $+8.4 \text{ kJ mol}^{-1}$, respectively in a dilute aqueous environment versus the SHE. While both are able to catalyze the HER through a marginally endergonic reaction the most thermodynamically favourable pathways differed between the complexes. In particular, the most thermodynamically favourable pathway for the formation of H_2 by $^{\text{CN}}\text{Ox}$ involves an EECC mechanism whereas for $^{\text{NH}_2}\text{Ox}$ the most thermodynamically favourable pathway occurs via an ECCE mechanism. From the results presented the choice of substituent on the alkene backbone significantly affects the reduction potential and reaction Gibbs energies of protonation. The considerably more positive reduction potential for the CN-complexes may offer a solution to the problems experimentally observed for the production of H_2 .

Keywords

Hydrogen Evolution Reaction, HER Catalysts, Alternative Fuels, Diselenolene, Density Functional Theory

Introduction

Increasing levels of greenhouse gases in our atmosphere threatens our planet as a result of climate change.¹ A main component of greenhouse gases is carbon dioxide and is a primary product of fossil-fuel consumption which is required for the planet's energy demands. In fact 80% of the world's energy consumption is derived from the burning of fossil fuels.²⁻⁵ Based on current emission levels of CO₂ into our atmosphere the Earth is on track for continued global temperature increases. Importantly, it has been stated that an increase of 2 °C in Earth's average temperature is considered a benchmark where the risk of climate change becomes threatening.⁶ Based on the current levels of CO₂ emissions the probability of reaching this 2 °C benchmark by 2100 is 88%!⁷ Thus, to prevent this increase of 2 °C urgent action is required. Such action involves reduced fossil fuel consumption and the development of renewable energy sources to reduce the amount of CO₂ emitted into our atmosphere.^{1-2, 6-9}

As noted above fossil fuels are a large contributor to carbon dioxide emissions, however, fossil fuels are a non-renewable fuel source, thus regardless of environmental concerns we must transition to renewable energy sources or risk running out of fossil fuels.⁶⁻⁹ Currently there are several alternative energy sources available such as wind, solar and tidal. The most viable path for large-scale growth of alternative energy sources involves solar energy conversion, and specifically the photocatalytic splitting of water to form molecular hydrogen to be used as an alternative fuel.^{2, 10-12} While hydrogen is the most abundant element in the universe, molecular hydrogen itself is not present on earth in significant amounts and must be produced from a hydrogen-containing source, such as water. Electrolysis of water allows for conversion of electricity into chemical energy, allowing for separation of hydrogen from water. However, presently there are limited methods available for hydrogen fuel production that are efficient and do so at relatively low costs. As a means to minimize costs, research is under way in the development of various catalysts using base-metals such as copper, nickel, iron and cobalt.¹³

However, many catalysts investigated for the production of molecular hydrogen decompose over time due to the hydrogenation of the ligands.¹⁴

Of the various base-metal containing catalysts studied in the past, complexes containing dithiolene ligands showed favourable properties for the photocatalytic splitting of water to form hydrogen gas.^{2, 13-14} In particular, in the production of H₂ by dithiolene containing catalysts the unsaturated 1,2-dithiolene ligands are less susceptible to hydrogenation, which, as discussed above, resulted in the decomposition of previous catalysts.^{13, 15} Since metal-dithiolene complexes are capable of undergoing multi-electron processes it has been proposed that the generation of hydrogen occurs through stepwise one-electron transfers and protonations.^{2, 15} The unique chemistry of dithiolene containing complexes is a result of the noninnocent interaction between metal and ligands.¹⁶ Dithiolene ligands are in fact prototypical redox-noninnocent ligands and undergo reversible redox reactions when coupled to a metal. An advantage of such redox-active ligands is that by varying the R-groups attached to the ligand properties of the complex can be tuned for a specific application.^{13, 15}

Analogous to the dithiolene ligands are the diselenolene ligands. Recent research has compared the chemistry of dithiolene and diselenolene containing complexes and has shown that both have very similar geometrical and chemical properties.¹⁷⁻²⁰ While, this past work has found that the nature of chalcogen atoms does not strongly affect the chemistry of such complexes, subtle differences do exist between dithiolene and diselenolene complexes. For instance, the diselenolene complexes are found to have a smaller HOMO-LUMO energy gap than analogous dithiolene complexes and are thus expected to have a slight increase in kinetic reactivity for electron transfer processes.^{17, 20}

Recently, for NiFe-hydrogenases when the ligating cys was changed to sec-cys an improvement in the hydrogen evolution reaction (HER) was observed as a result of changing the S-atom to a Se-atom.²¹⁻²⁴ This improvement was suggested to be due to the higher nucleophilicity of the selenocysteine and the lower pK_a of the –SeH moiety.²¹⁻²⁴ Similarly, experimental research has shown that in the case of Ni-bis(benzene-1,2,4,5-selenolate) polymers replacement of S with

Se reduces the overpotential needed for the HER, moreover, the selenium catalysts showed significant improvement in durability of the catalysts under prolonged reductive acidic conditions.²⁵

In the present work the 1,2-diamine-diselenolene and 1,2-dicyano-diselenolene nickel complexes were studied using Density Functional Theory (DFT) calculations to investigate the HER of two Ni-bis(diselenolene) complexes. The choice of moieties attached to the ligands also allows the investigation into how an electron donating or electron withdrawing moiety affects the thermodynamics of reduction and protonation. The R-groups chosen included the strong electron donating $-NH_2$ group, and the strong electron withdrawing $-CN$ group. The structures of the different nickel complexes studied are shown in **Scheme 1**.

Methods

The Gaussian 09 software suite was used to perform all calculations. Geometry optimizations were performed at the B3LYP/6-31G(d) level of theory.²⁶⁻³² Single point energies were obtained at the IEFPCM-M06/6-311+G(2df,p) level of theory where the IEFPCM approach was used to model the presence of solvent on the reaction where water was chosen as the solvent.³³⁻³⁹ Single point energies were corrected to Gibbs energies by adding the Gibbs corrections calculated by performing frequency calculations at the B3LYP/6-31G(d) level of theory on the optimized geometries. The M06 functional was chosen due to past work which has shown the accuracy of the functional when calculating reduction potentials of diselenolene complexes.^{19, 40-41} The M06 functional is a meta-hybrid functional for general-purpose applications, and has been shown to be suitable for applications in transition metal chemistry giving better performance than B3LYP for main-group thermochemistry, barrier heights, and non-covalent interactions.³⁸⁻³⁹

We have considered the assembly of two protons and two electrons to form H_2 via a series of stepwise electron transfers and proton transfers. Using the Gibbs corrections and single point

energies the relative reduction potentials (versus the SHE) (**Eq. 1 - 3**) and protonation energies in aqueous solution (**Eq. 4 and 5**) were obtained.

$$\Delta_r G_s^0 = \mu_{298\text{k}}^{0,\text{g}}(\text{RED}) + \Delta G_s^0(\text{RED}) - \mu_{298\text{k}}^{0,\text{g}}(\text{OX}) - \Delta G_s^0(\text{OX}) - \mu_{298\text{k}}^{0,\text{SHE}}(e^-) \quad (2)$$

$$E^0 = -\Delta_r G_s^0 / F \quad (3)$$

$$\Delta_r G_s^0 = \mu_{298\text{k}}^{0,\text{g}}(\text{Acid}) + \Delta G_s^0(\text{Acid}) - \mu_{298\text{k}}^{0,\text{g}}(\text{Base}) - \Delta G_s^0(\text{Base}) - \mu_{298\text{k}}^{0,\text{aq}}(\text{H}^+) \quad (5)$$

$\mu_{298\text{k}}^{0,\text{g}}(\text{X})$ is the chemical potential in gas phase at 298 K for species X and $\Delta G_s^0(\text{X})$ is the bulk energy of solvation. In accordance to the work by Llano and Eriksson⁴² the chemical potential of the electron ($\mu_{298\text{k}}^{0,\text{SHE}}(e^-)$) is $-418.5 \pm 2.1 \text{ kJ mol}^{-1}$ setting the calculated reduction potentials relative to the SHE whereas the chemical potential of a proton in a dilute aqueous environment ($\mu_{298\text{k}}^{0,\text{aq}}(\text{H}^+)$) is $-1124.2 \pm 0.8 \text{ kJ mol}^{-1}$.

The models used in the study are shown in **Scheme 1**.

Results and Discussion

It has been previously been proposed that H_2 production by a series of Ni-complexes occurs after two electrons and two protons have been added to the metal complex.² In particular, for a series of Ni-dithiolene complexes Das et al.² proposed that an ECEC mechanism (E = electron transfer; C = chemical step) in the formation of H_2 where a ligand is first protonated followed by protonation of the Ni atom to form a metal-hydride.² For production of H_2 by metal selenolate polymers Downes and Marinescu²⁵ proposed that depending on the experimental conditions two possible mechanisms exist for H_2 production. At more positive potentials an ECCE mechanism is

followed whereas at more negative potentials an ECEC mechanism is followed, however, no metal-hydride intermediate is proposed to exist in either mechanism.

In the present study many possible mechanisms have been considered. The reaction Gibbs energies for protonation and relative the reduction potentials for the amine and cyano-containing Ni-bis(diselenolene) complexes (**Scheme 1**) are provided in **Figures 1** and **2**.

For the oxidized species $^{\text{NH}_2}\text{Ox}$ and $^{\text{CN}}\text{Ox}$ two possible sites of protonation exist. The first site of protonation is a ligating selenium atom which leads to Ox-H_a , whereas the second protonation site is the central Ni atom and leads to Ox-H_b . From **Figure 1** the formation of Ox-H_a in a dilute aqueous environment is endergonic for both the amine and cyano complexes, where addition of a proton to a selenium atom of $^{\text{NH}_2}\text{Ox}$ and $^{\text{CN}}\text{Ox}$ was found to occur with $\Delta_r G_s^\circ = 42.1 \text{ kJ mol}^{-1}$ and $\Delta_r G_s^\circ = 188.7 \text{ kJ mol}^{-1}$, respectively. Therefore, in a dilute aqueous environment protonation of either complex is thermodynamically unfavourable, however, it is noted that protonation of $^{\text{NH}_2}\text{Ox}$ is considerably less endergonic than the protonation of $^{\text{CN}}\text{Ox}$ ($\Delta\Delta_r G_s^\circ = 146.6 \text{ kJ mol}^{-1}$). Regarding the protonation of the Ni-atom it was found that the formation of $^{\text{NH}_2}\text{Ox-H}_b$ is an endergonic process with a reaction Gibbs energy ($\Delta_r G_s^\circ$) of $107.0 \text{ kJ mol}^{-1}$ (**Figure 1**). Due to the considerable cost in reaction Gibbs energy for protonation in a dilute aqueous environment the protonation of the central Ni-atom of $^{\text{NH}_2}\text{Ox}$ seems unlikely. Regarding $^{\text{CN}}\text{Ox-H}_b$, at the B3LYP/6-31G(d) level of theory the proton was found to migrate from the central Ni-atom to a ligating Se-atom. Thus, at the present level of theory it appears that $^{\text{CN}}\text{Ox-H}_b$ is not a stable intermediate. The preferential protonation of the ligand versus the central Ni-atom supports the proposed mechanism of Das et al.² as well as Downes and Marinescu²⁵ where the first proton is added to the ligand.

Following the addition of a proton the reduction potentials for the redox couples $^{\text{CN}}\text{Ox-H}_a/^{\text{CN}}\text{Red-H}_a$ and $^{\text{NH}_2}\text{Ox-H}_a/^{\text{NH}_2}\text{Red-H}_a$ were calculated to be 1.99 V and 0.26 V for, respectively. Therefore, both redox couples are more oxidizing than the SHE. As stated above a stable intermediate of the cyano derivative $^{\text{CN}}\text{Red-H}_b$ could not be optimized at the present level of

theory. In regard to the $^{\text{NH}_2}\text{Ox-H}_b/^{\text{NH}_2}\text{Red-H}_b$ redox couple the calculated reduction potential is -0.06 V and is therefore marginally more reducing than the SHE.

If we consider the alternative of first reducing the oxidized species followed by protonation the reduction potentials relative to the SHE for the $^{\text{NH}_2}\text{Ox}/^{\text{NH}_2}\text{Red}$ and $^{\text{CN}}\text{Ox}/^{\text{CN}}\text{Red}$ redox couples are calculated to be -0.27 V and $+1.28$ V (**Figure 1**), respectively. Thus, relative to the SHE the reduction of the cyano-containing species is thermodynamically favourable whereas for the amine-containing complex reduction is not thermodynamically. Given the values in **Figure 1** the reduction of $^{\text{NH}_2}\text{Ox}$ and $^{\text{CN}}\text{Ox}$ is more likely than protonation at the present level of theory. Following the electron transfer, protonation of $^{\text{NH}_2}\text{Red}$ and $^{\text{CN}}\text{Red}$ can occur at a ligand Se atom or the central Ni atom. As stated above the intermediate $^{\text{CN}}\text{Red-H}_b$ did not exist at the present level of theory and therefore does not appear to be a stable intermediate in the formation of H_2 . However, protonation of $^{\text{NH}_2}\text{Red}$ to form $^{\text{NH}_2}\text{Red-H}_b$ occurs with a reaction Gibbs energy ($\Delta_r G_s^\circ$) of 86.0 kJ mol $^{-1}$ and therefore represents a considerable endergonic step in the formation of H_2 . With the protonation of a ligating Se-atom reaction Gibbs energies ($\Delta_r G_s^\circ$) of 120.8 kJ mol $^{-1}$ and -9.1 kJ mol $^{-1}$ for $^{\text{CN}}\text{Red}$ and $^{\text{NH}_2}\text{Red}$ were calculated, respectively.

The reaction Gibbs energies and relative reduction potentials for the second protonation and second reduction are provided in **Figure 2**, respectively. It is noted that Red-H_b is not included in **Figure 2**.

Due to the high energetic cost to protonate $^{\text{CN}}\text{Red}$ (**Figure 2**) the possibility of a second reduction prior to protonation was considered; i.e., an EECC mechanism was considered. For purposes of completeness the possibility of a second reduction prior to formation of $^{\text{NH}_2}\text{Red-H}_a$ was also considered. For the $^{\text{CN}}\text{Red}/^{\text{CN}}2\text{Red}$ and $^{\text{NH}_2}\text{Red}/^{\text{NH}_2}2\text{Red}$ redox couples the relative reduction potentials are calculated to be 0.24 V and -0.69 V, respectively. Thus, relative to the SHE only reduction of the $^{\text{CN}}\text{Red}/^{\text{CN}}2\text{Red}$ redox couples is thermodynamically favourable whereas reduction of the $^{\text{NH}_2}\text{Red}/^{\text{NH}_2}2\text{Red}$ redox couples is not. From **Figure 1** given that the protonation of $^{\text{NH}_2}\text{Red}$ in a dilute aqueous environment to form $^{\text{NH}_2}\text{Red-H}_a$ occurs with a reaction Gibbs energy of -9.1 kJ mol $^{-1}$ it is unlikely that $^{\text{NH}_2}2\text{Red}$ represent a stable intermediate in the

formation of H_2 in a dilute aqueous environment where the reducing electrons are coming from a SHE.

From **Figure 2** the reduction potential for the $^{NH_2}Red-H_a/^{NH_2}2Red-H_a$ redox couple was calculated to be -0.50 V relative to the SHE, and is therefore not a thermodynamically favourable process when the reducing electrons are gained from the SHE. For the $^{CN}Red-H_a/^{CN}2Red-H_a$ redox couple a reduction potential of $+0.95$ V was calculated. However, given the considerable cost for formation of $^{CN}Red-H_a$ (**Figure 2**) it is unlikely that $^{CN}2Red-H_a$ is formed.

Given the negative reduction potential of -0.50 V versus the SHE for the $^{NH_2}Red-H_a/^{NH_2}2Red-H_a$ redox couple the protonation of $^{NH_2}Red-H_a$ was considered prior to a second reduction; i.e., an ECCE mechanism was considered. Regarding $^{NH_2}Red-H_a$, four possible sites of protonation exist, for purposes of completeness the CN-derivative was also considered. As seen in **Figure 2** addition of a proton to the central nickel atom results in the formation of $Red-H_c$ and occurs with a reaction Gibbs energy ($\Delta_r G_s^\circ$) of 252.1 kJ mol $^{-1}$ and 165.4 kJ mol $^{-1}$ for $^{CN}Red-H_c$ and $^{NH_2}Red-H_c$, respectively. Thus, given the considerable endergonicity for formation of $^{CN}Red-H_c$ and $^{NH_2}Red-H_c$ it is unlikely the formation of H_2 proceeds through such an intermediate. With the addition of the proton to the *cis* selenium atom on the adjacent diselenolene ligand forming $^{CN}Red-H_d$ and $^{NH_2}Red-H_d$ the reaction Gibbs energy ($\Delta_r G_s^\circ$) was calculated to be 164.0 kJ mol $^{-1}$ and 65.7 kJ mol $^{-1}$, respectively. With the addition of a proton to the *cis* selenium atom resulting in a doubly protonated diselenolene ligand occurs with reaction Gibbs energies of 154.7 kJ mol $^{-1}$ and 46.4 kJ mol $^{-1}$ resulting in the formation of $^{CN}Red-H_e$ and $^{NH_2}Red-H_e$, respectively. Lastly protonation of the *trans* Se-atom reaction Gibbs energies of 165.3 kJ mol $^{-1}$ and 67.7 kJ mol $^{-1}$ were calculated for $^{CN}Red-H_e$ and $^{NH_2}Red-H_e$, respectively. Thus, given the negative reduction potential of -0.50 V versus the SHE for the $^{NH_2}Red-H_a/^{NH_2}2Red-H_a$ redox couple in a dilute aqueous environment the protonation of $^{NH_2}Red-H_a$ to form $^{NH_2}Red-H_e$ is marginally thermodynamically favoured, and therefore $^{NH_2}Red-H_e$ is more favoured to form than $^{NH_2}2Red-H_a$. With the formation of $^{NH_2}Red-H_e$ reduction to $^{NH_2}2Red-H_e$ occurs at a relative reduction potential of -0.26 V. However, from **2** given the very similar costs in Gibbs energy for formation

of $^{\text{NH}_2}\text{Red-H}_e$ and $^{\text{NH}_2}2\text{Red-H}_a$ the protonation of $^{\text{NH}_2}2\text{Red-H}_a$ to form $^{\text{NH}_2}2\text{Red-H}_d$ was considered. As seen in **Figure 2** this occurs as an exergonic process with a reaction Gibbs energy ($\Delta_r G_s^\circ$) of -9.2 kJ mol^{-1} . Moreover, formation of $^{\text{NH}_2}2\text{Red-H}_f$ also occurs as an exergonic process with a reaction Gibbs energy ($\Delta_r G_s^\circ$) of $-16.9 \text{ kJ mol}^{-1}$. While formation of $^{\text{NH}_2}\text{Red-H}_e$ is marginally more favourable than formation of $^{\text{NH}_2}2\text{Red-H}_a$ it might be expected that under slightly reducing conditions in a dilute aqueous environment $^{\text{NH}_2}2\text{Red-H}_a$ is likely first formed followed by protonation to form $^{\text{NH}_2}2\text{Red-H}_f$. However, in acidic conditions the reaction would most likely proceed through the formation of $^{\text{NH}_2}\text{Red-H}_e$ followed by reduction to form the complex, $^{\text{NH}_2}2\text{Red-H}_e$. Regarding the CN-derivative given the energies and reduction potentials provided in **Figures 1** and **2** the most likely pathway involves two one-electron reductions prior to protonation.

From **Figures 1** and **2** the lowest energetic pathway for double protonation and double reduction of $^{\text{CN}}\text{Ox}$ and $^{\text{NH}_2}\text{Ox}$ are shown in **Figures 3** and **4**. Regarding $^{\text{CN}}\text{Ox}$ in a dilute aqueous environment versus the SHE the pathway with the lowest energetic involves an EECC mechanism and results in the formation of $^{\text{CN}}2\text{Red-H}_d$. From the energies provided in **Figure 3** the formation of $^{\text{CN}}2\text{Red-H}_d$ with an overall reaction Gibbs energy of $-11.8 \text{ kJ mol}^{-1}$.

In the case of $^{\text{NH}_2}\text{Ox}$ in a dilute aqueous environment versus the SHE the lowest energetic pathway involves an ECCE mechanism and results in the formation of 2Red-H_e with an overall reaction Gibbs energy of $+88.4 \text{ kJ mol}^{-1}$ (**Figure 4**). Thus, at the IEFPCM-M06/6-311+G(2df,p)//B3LYP/6-31G(d) level of theory the most thermodynamically favourable pathway for formation of H_2 in the presence of $^{\text{NH}_2}\text{Ox}$ and $^{\text{CN}}\text{Ox}$ occurs via an ECCE and EECC mechanism, respectively. As noted above it has been proposed that generation of hydrogen occurs through stepwise electron transfers and protonations since metal-dithiolene complexes are capable of undergoing multi-electron processes. The results presented herein support such a mechanism. Interestingly, in regards to the work by Downes and Marinescu²⁵ it was proposed that for a series of Ni-bis(benzene-1,2,4,5-selenolate) polymers at more positive potentials an ECCE mechanism is followed. At more negative potentials ECEC mechanism occurs. As noted

above Das et al.² proposed that an ECEC mechanism (E = electron transfer; C = chemical step) in the formation of H₂ where a ligand is first protonated followed by protonation of the Ni-atom to form a metal-hydride.² The complex investigated by Das et al.² was the unsubstituted Ni-(bis(benzene-dithiolene)) and therefore the ligand would be slightly electron donating. From **Figures 1** and **2** only the amine-containing complex is able to form the Ni-H species at the present level of theory, however, due to the considerable energetic cost for the formation of ^{NH}₂2Red-H_c it seems that, at the present level of theory, a Ni-H intermediate is unlikely to exist in the formation of H₂ in a dilute aqueous environment versus the SHE.

It is noted that in the work of Das et al. an issue with the Ni-bis(benzenedithiolene) was the need for very reducing conditions.² In the photocatalytic generation of H₂ from Ni-bis(benzenedithiolene) the reducing ability of the reduced fluorescein (Fl⁻) to reduce the Ni-complexes was insufficient for the production of H₂ gas.² From the values provided in **Figures 1** and **2** it is clear the choice of substituent on the alkene backbone both affects the reduction potential and reaction Gibbs energies of protonation. The ability of the moieties to affect the reduction potentials of diselenolene complexes has been previously investigated.^{17, 19-20, 41} The considerably more positive reduction potential for the Cyano complexes may offer a solution to the problems involved in the production of H₂ as seen by Das et al.²

With double reduction and double protonation the last step in the mechanism is formation of H₂. For purposes of completeness the reaction Gibbs energies for the formation of H₂ from 2Red-H_d, 2Red-H_e and 2Red-H_f are provided in **Figure 5**. For the cyano complexes the only doubly-reduced and doubly-protonated complex that results in the formation of H₂ via an exergonic step is ^{CN}2Red-H_e, whereas all amine-containing complexes undergo an exergonic process. Regarding the CN-derivative if we consider the most thermodynamically favourable pathway from **Figure 3** the formation of H₂ occurs with an overall reaction Gibbs energy of +8.7 kJ mol⁻¹ and proceeds through ^{CN}2Red-H_d to reform ^{CN}Ox and H₂(g). Therefore, the formation of H₂ with the use of the CN-containing catalyst is marginally endergonic.

Similarly, if we consider the most thermodynamically favourable pathway from **Figure 4** the formation of H_2 likely passes through the intermediate $^{NH_2}2Red-H_e$ and occurs with an overall reaction Gibbs energy of $+8.4 \text{ kJ mol}^{-1}$. Therefore, the overall Gibbs energy for the formation of H_2 , is the essentially identical regardless of the choice of moiety attached to the alkene backbone of the diselenolene ligand, however, the thermodynamics of each individual step differs greatly depending on moiety chosen. In particular, from the results presented the choice of the cyano-moieties results in complexes that are more oxidizing but that are more difficult to protonate whereas the choice of amine-moieties results in compounds that are reducing versus the SHE yet thermodynamically favourable to being protonated in a dilute aqueous environment.

Conclusion

In the present manuscript the thermodynamics for the production of H_2 by ^{CN}Ox and ^{NH_2}Ox was investigated. In particular, the thermodynamics for many reactions involving sequential one-electron reductions or protonation steps were investigated. From the results obtained at the IEFPCM-M06/6-311+G(2df,p)//B3LYP/6-31G(d) level of theory, it was found that both the ^{CN}Ox and ^{NH_2}Ox catalyze the formation of $H_2(g)$ with overall Gibbs reaction energies of $+8.7 \text{ kJ mol}^{-1}$ and $+8.4 \text{ kJ mol}^{-1}$, respectively in a dilute aqueous environment versus the SHE. Thus, both catalysts catalyze the formation of H_2 via a marginally endergonic pathway. However, in regards to ^{CN}Ox the most thermodynamically favourable pathway involves an EECC mechanism whereas in the case of ^{NH_2}Ox the most thermodynamically favourable pathway occurs via an ECCE mechanism. From the results presented the choice of substituent on the alkene backbone considerably affects thermodynamics of the individual steps. Importantly, the considerably more positive reduction potential for the CN-complexes may offer a solution to the problems involved in the production of H_2 seen in past experimental work.

Acknowledgements

EACB thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding. EACB and BTAB thank WESTGRID, SHARCNET and Compute Canada for computational resources.

Supporting Information

The xyz coordinates of the complexes discussed in the present article are provided in **Table S1**.

References:

- (1) Peters, G. P.; Andrew, R. M.; Boden, T.; Canadell, J. G.; Ciais, P.; Le Quéré, C.; Marland, G.; Raupach, M. R.; Wilson, C., *Nat. Clim. Change* **2013**, 3, 4.
- (2) Das, A.; Han, Z.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R., *ACS Catal.* **2015**, 5 (3), 1397.
- (3) U.S. Department of Energy, Energy Information Administration: Washington, DC, 2013; pp 55.
- (4) U. S. Department of Energy, Energy Information Administration: Washington, DC, 2013; pp 1.
- (5) Hoffert, M. I.; Caldeira, K.; Jain, A. K.; Haites, E. F.; Harvey, L. D. D.; Potter, S. D.; Schlesinger, M. E.; Schneider, S. H.; Watts, R. G.; Wigley, T. M. L.; Wuebbles, D. J., *Nature* **1998**, 395 (6705), 881.
- (6) Sottong, J.; Broomfield, M.; MacCarthy, J.; Misra, A.; Thistlethwaite, G.; Watterson, J. In *Still Only One Earth: Progress in the 40 Years Since the First UN Conference on the Environment*, The Royal Society of Chemistry 2015; pp 34.

- (7) Capellan-Perez, I.; Arto, I.; Polanco-Martinez, J. M.; Gonzalez-Eguino, M.; Neumann, M. B., *Energy Environ. Sci.* **2016**, 9 (8), 2482.
- (8) Kahn, B. 2017.
- (9) Jakob, M.; Hilaire, J., *Nature* **2015**, 517 (7533), 150.
- (10) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J., *Inorg. Chem.* **2005**, 44 (20), 6802.
- (11) Bard, A. J.; Fox, M. A., *Acc. Chem. Res.* **1995**, 28 (3), 141.
- (12) Lewis, N. S.; Nocera, D. G., *Proc. Nat. Acad. Sci. U.S.A.* **2006**, 103 (43), 15729.
- (13) Zarkadoulas, A.; Field, M. J.; Papatriantafyllopoulou, C.; Fize, J.; Artero, V.; Mitsopoulou, C. A., *Inorg. Chem.* **2016**, 55 (2), 432.
- (14) McNamara, W. R.; Han, Z.; Yin, C.-J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R., *Proc. Natl. Acad. Sci. U.S.A.* **2012**, 109 (39), 15594.
- (15) Eisenberg, R.; Gray, H. B., *Inorg. Chem.* **2011**, 50 (20), 9741.
- (16) Davison, A.; Edelstein, N.; Holm, R. H., *J. Am. Chem. Soc.* **1964**, 86, 2799.
- (17) Bushnell, E. A. C.; Adams, M. R.; Boyd, R. J., *Struct. Chem.* **2017**.
- (18) Bushnell, E. A. C., *Can. J. Chem.* **2016**, 94 (12), 1127.
- (19) Bushnell, E. A. C.; Boyd, R. J., *J. Phys. Chem. A* **2015**, 119 (5), 911.
- (20) Bushnell, E. A. C.; Boyd, R. J., *Int. J. Quantum Chem.* **2016**, 116 (5), 369.
- (21) Wombwell, C.; Caputo, C. A.; Reisner, E., *Acc. Chem. Res.* **2015**, 48 (11), 2858.
- (22) Figliola, C.; Male, L.; Horton, P. N.; Pitak, M. B.; Coles, S. J.; Horswell, S. L.; Grainger, R. S., *Organometallics* **2014**, 33 (17), 4449.
- (23) Wombwell, C.; Reisner, E., *Dalton Trans.* **2014**, 43 (11), 4483.
- (24) Wombwell, C.; Reisner, E., *Chem. Eur. J.* **2015**, 21 (22), 8096.
- (25) Downes, C. A.; Marinescu, S. C., *ACS Catal.* **2017**, 7 (1), 848.
- (26) Becke, A. D., *J. Chem. Phys.* **1993**, 98, 1372.
- (27) Becke, A. D., *J. Chem. Phys.* **1993**, 98 (7), 5648.
- (28) Handy, N. C.; Cohen, A. J., *Mol. Phys.* **2001**, 99 (5), 403.

- (29) Lee, C. T.; Yang, W. T.; Parr, R. G., *Phys. Rev. B* **1988**, *37* (2), 785.
- (30) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., *J. Phys. Chem.* **1994**, *98* (45), 11623.
- (31) Vosko, S. H.; Wilk, L.; Nusair, M., *Can. J. Phys.* **1980**, *58* (8), 1200.
- (32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachar, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01*, Gaussian, Inc.: Wallingford CT, 2010.
- (33) Cances, E.; Mennucci, B.; Tomasi, J., *J. Chem. Phys.* **1997**, *107* (8), 3032.
- (34) Mennucci, B.; Cances, E.; Tomasi, J., *J. Phys. Chem. B* **1997**, *101* (49), 10506.
- (35) Mennucci, B.; Tomasi, J., *J. Chem. Phys.* **1997**, *106* (12), 5151.
- (36) Tomasi, J.; Mennucci, B.; Cammi, R., *Chem. Rev.* **2005**, *105* (8), 2999.
- (37) Tomasi, J.; Mennucci, B.; Cances, E., *J. Mol. Struct. THEOCHEM* **1999**, *464* (1-3), 211.
- (38) Zhao, Y.; Truhlar, D. G., *Acc. Chem. Res.* **2008**, *41* (2), 157.
- (39) Zhao, Y.; Truhlar, D. G., *Theor. Chem. Acc.* **2008**, *120* (1-3), 215.
- (40) Bushnell, E. A. C.; Burns, T. D.; Boyd, R. J., *J. Chem. Phys.* **2014**, *140* (18), 18A519.
- (41) Bushnell, E. A. C.; Burns, T. D.; Boyd, R. J., *Phys. Chem. Chem. Phys.* **2014**, *16* (22), 10897.
- (42) Llano, J.; Eriksson, L. A., *J. Chem. Phys.* **2002**, *117* (22), 10193.

Scheme 1: The oxidized structures of the cyano ($\text{CN}^{\text{N}}\text{O}_x$) and amine ($\text{NH}_2^{\text{N}}\text{O}_x$) containing Ni-bis(diselenolene) complexes investigated in the present work.

Figure 1: The Gibbs energies ($\Delta_r G_s^\circ$ in kJ mol^{-1}) and relative reduction potentials (E° in V) for the first electron transfer and protonation steps in the formation of H_2 by Ni-bis(diselenolene) complexes investigated herein. The reaction Gibbs energies and relative reduction potentials provided in terms of moiety attached to the alkene backbone is indicated by the CN or NH_2 in parentheses.

Figure 2: The Gibbs energies ($\Delta_r G_s^\circ$ in kJ mol^{-1}) and relative reduction potentials (E° in V) for the second electron transfer and second protonation steps in the formation of H_2 by Ni-bis(diselenolene) complexes investigated herein. The reaction Gibbs energies and relative reduction potentials provided in terms of moiety attached to the alkene backbone is indicated by the CN or NH_2 in parentheses.

Figure 3. The lowest energetic pathway for double protonation and double reduction of $^{\text{CN}}\text{Ox}$ forming $^{\text{CN}}2\text{Red-H}_d$. The energies provided are strictly related to the thermodynamics of the reaction.

Figure 4. The lowest energetic pathway for double protonation and double reduction of $^{\text{NH}_2}\text{Ox}$ forming $^{\text{NH}_2}2\text{Red-H}_d$. The energies provided are strictly related to the thermodynamics of the reaction.

Figure 5. The Gibbs energies ($\Delta_r G_s^\circ$ in kJ mol^{-1}) for the formation of $\text{H}_2(\text{g})$ by Ni-bis(diselenolene) complexes. The reaction Gibbs energies provided are given in terms of moiety attached to the alkene backbone of the diselenolene ligand where the moiety is indicated by $\text{R} = \text{CN}$ or NH_2