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Proton reduction reaction catalyzed by homoleptic nickel bis-1,2-dithiolate complexes: Experimental and theoretical mechanistic investigations

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Abstract

A series of homoleptic monoanionic nickel dithiolene complexes [Ni(bdt)₂](NBu₄), [Ni(tdt)₂](NBu₄), and [Ni(mnt)₂](NBu₄) containing the ligands benzene-1,2-dithiolate (bdt²⁻), toluene-3,4-dithiolate (tdt²⁻) and maleonitriledithiolate (mnt²⁻), respectively, have been employed as electrocatalysts in the hydrogen evolution reaction with trifluoroacetic acid as proton source in acetonitrile. All complexes were active catalysts with TONs reaching 113, 158 and 6 for [Ni(bdt)₂](NBu₄), [Ni(tdt)₂](NBu₄), and [Ni(mnt)₂](NBu₄), respectively. Faradaic yield for hydrogen evolution reaction reaches 88 % for **2**⁻, which also displays the minimal overpotential requirement value (467 mV) within the series. Two pathways for H₂ evolution can be hypothesized that differ on the sequence of protonation and reduction steps. DFT calculations are in agreement with experimental data and indicate that protonation at sulfur follows reduction to the dianion. Hydrogen evolves from the direduced-diprotonated form via a highly distorted nickel hydride intermediate. The effects of acid strength and concentration in the hydrogen-evolving mechanism are also discussed.

Keywords

dithiolene; nickel; electrocatalysis; DFT; non-innocent ligand; dithiolate; hydrogen evolution

1 Introduction

The occurrence and importance of nickel in nature and living organisms [1] has led to the increasing interest of coordination chemists in the preparation and study of nickel complexes that resemble the nickel coordination environments found in nature. In this context, great

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effort has been put into the preparation, characterization, and application in catalysis of complexes that mimic the active sites of [NiFe] or [FeFe] hydrogenases [2–4], and that catalyze the reduction of protons to hydrogen and vice versa.

The active site of [NiFe] hydrogenase contains a nickel ion in a sulfur-rich environment provided by four cysteine residues, two of them bridging to an organometallic iron moiety [5]. Detailed work by several groups [6–15] reveals the importance of sulfur atoms adjacent to nickel ions if hydrogen evolution is to take place. Examination of the literature regarding nickel complexes coordinated to sulfur atoms immediately shows the recurrence of dithiolene and dithiolate ligands. More specifically, complexes of 1,2-dithiolenes have been the subject of both experimental and theoretical work [16–22] since early reports of their synthesis and properties [23,24]. This is because they exhibit non-linear optical properties [18,25,26], are of bioinorganic interest due to their similarity with molybdenum enzymes [27], and have found application in dye-sensitized solar cells as chromophores [28–30], as catalysts in hydrogen evolution reactions [31–34], and as metallodrugs [35–37].

Due to the unique electronic properties of dithiolene ligands, the electron density of metal-dithiolene complexes is delocalized over the metal-sulfur core, which allows electron storage and access to several stable anionic oxidation states. These properties have led to the investigation of metal dithiolenes as catalysts in the reductive side of water splitting [27,32–34,38–42]. More recently, the groups of Eisenberg and Holland reported Co dithiolenes to be very active catalysts for the photocatalytic and electrocatalytic hydrogen evolution reactions [43,44], followed by reports on similar Mo and Ni benzene-1,2-dithiolate complexes [45,46]. In addition, Fontecave and coworkers described W and Mo oxo-dithiolene complexes active for H₂ evolution [27,47] and, more recently, Kochem et al. [48] reported on the preparation and study of a mixed-ligand Ni dithiolene complex with a diphosphine ligand bearing a nitrogen atom as proton relay. Finally, a bimetallic, bio-inspired compound incorporating a ferrocene moiety in a nickel benzene-dithiolate environment [49] has also been reported to catalyze proton reduction with a calculated TOF of 1240 s⁻¹ at low acid concentrations and an overpotential requirement of 265 mV.

As well as their electronic properties, the perfectly planar nature of the aromatic dithiolene complexes has been used to prepare materials that act as cathodes in the hydrogen evolution reaction [50]. In this context, Clough et al. reported [51,52] the application of a robust Co-dithiolene nanosheet that acts as a multi-site catalyst for the hydrogen evolution reaction.

Following our initial report on H₂ evolution catalyzed by a series of bis-aryldithiolene nickel complexes [53], the intriguing behavior of nickel bis-dithiolene complexes [54] under reductive conditions in the presence of acid with respect to the hydrogen evolution reaction prompted us to investigate the reactivity of three nickel dithiolene complexes [Ni(bdt)₂](NBu₄) (**1**(NBu₄), bdt²⁻ = benzene-1,2-dithiolate, NBu₄⁺ = tetrabutylammonium), [Ni(tdt)₂](NBu₄) (**2**(NBu₄), tdt²⁻ = toluene-3,4-dithiolate) and [Ni(mnt)₂](NBu₄) (**3**(NBu₄), mnt²⁻ = maleonitriledithiolate) as catalysts for H₂ evolution (Scheme 1). We report here on their activity, detail their catalytic mechanism, with the support of quantum chemical methods, and highlight the role of acid in proton reduction catalysis versus decomposition processes.

2 Experimental

General considerations

Reagents and solvents were purchased from Aldrich, Alfa Aesar, Merck or Fisher and used as received unless otherwise noted.

UV-Vis spectra were recorded with Hitachi U-2000 and Varian Cary 3E spectrophotometers in 1.0 cm quartz cuvettes.

Electrochemistry

Electrochemical experiments were performed using an AFCBP1 Pine Instrument Company and Bio-Logic SP300 potentiostat. Cyclic voltammograms were performed in a two-compartment cell with a glassy carbon working electrode, an Ag/AgCl (KCl 3M) reference electrode and a platinum wire counter-electrode (located in the second compartment). The glassy carbon electrode was polished with diamond paste or alumina on a polishing cloth before each measurement. The solution was purged with argon or nitrogen gas prior to measurements. The measurements have been carried out in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. At the end of each experiment, sublimed ferrocene was added as an internal standard. Bulk electrolysis was performed in a two-compartment cell with a glassy carbon rod electrode ($\varnothing$ 10 mm, Neyco, Paris, France), an Ag/AgCl reference electrode and a platinum wire as counter-electrode (located in the second compartment). The headspace of the vial was analyzed at two-minute intervals in a Perkin Elmer Clarus 500 gas chromatograph using a previously described setup [55].

DFT studies

All quantum chemical calculations were done with a density functional theory (DFT) approach using the B3LYP functional and basis sets of triple-zeta (TZVP) quality. The ORCA program package (version 2.9.1) was employed for all electronic structure calculations [56]. Two approaches were employed for estimating the relative energies of different species and the energies of the various reactions. In the first, geometry optimizations were performed for all species in vacuum using the B3LYP functional and a TZVP basis set. Single point energy calculations were then performed on these optimized vacuum structures using the B3LYP functional and an extended TZVP basis set with extra polarization and diffuse functions. These single point calculations were performed in both vacuum and MeCN solvent using the COSMO implicit solvation method that ORCA implements [57]. In addition, normal mode calculations were performed at the vacuum optimized geometries using the B3LYP functional and original TZVP basis set to obtain the appropriate free energy contributions to the species energies. The latter were estimated as the sum of the single point vacuum energy, the solvation energy (the difference between the single point solvent and vacuum energies) and the free energy contribution from the normal mode calculations. This approach seems to be similar to that used by many workers, including that described in Konezny and co-workers [58]. In the second approach – performed as a check of the first – potential (rather than free) energies for the reactions were estimated by geometry optimizing all species in MeCN solvent using the B3LYP functional

and a TZVP basis set, followed by single point calculations in MeCN solvent with the same functional and the larger TZVP basis set. All the protonation energies were computed with respect to the CF₃COOH/CF₃COO[−] couple. The standard redox potential, E^0 , was calculated using the relation $E^0 = (-\Delta G^0)/nF - E_{ref}^0$, where G^0 is the free energy of reduction, n is the number of electrons being transferred, F is the Faraday constant and E_{ref}^0 is the absolute reduction potential of the ferrocene couple computed at the same level of theory.

Preparation of compounds

1[−] and **2[−]** were prepared by the reaction of either benzene-1,2-dithiol or toluene-3,4-dithiol with nickel chloride hexahydrate in absolute ethanol, as reported previously by Baker-Hawkes et al. [23], substituting potassium with sodium. **3[−]** was prepared by the iodine oxidation of the corresponding dianionic species, as reported earlier [59]. Analytical data for these complexes agree with those reported in the literature.

3 Results

Electrochemistry

The electrochemical behavior of all complexes has been examined in acetonitrile by cyclic voltammetry. In the case of **1[−]** and **2[−]**, one fully reversible redox process is observed and corresponds to the reduction of the monoanion to the dianionic compound (Figure 1). The reduction occurs at slightly negative potentials, −0.92 V vs Fc^{+/0} for **1[−]** and −0.95 V vs Fc^{+/0} for **2[−]**. The small negative shift (30 mV) for the reduction potential of **2[−]** compared to **1[−]** can be rationalized in terms of the electron donating effect of the methyl group that renders the sulfur atoms more electron-rich. Compound **3[−]** exhibits two well-defined redox waves, corresponding to formation of the one- and two-electron reduced species. Potential values of −0.08 V vs Fc^{+/0} and −2.00 V vs Fc^{+/0} correspond to the formation of the dianion and trianion, respectively. The electron-withdrawing effect of maleonitrile-dithiolate ligand for **3[−]** allows the accommodation of one more electron, leading to the formation of the trianionic species which is not observed for compounds **1[−]** and **2[−]** in the scanned potential range.

Electrocatalytic proton reduction

Trifluoroacetic acid (TFA, pK_a = 12.7 in MeCN [60]) has been employed as the proton source in hydrogen evolution experiments. Initial experiments with triethylammonium tetrafluoroborate (pK_a = 18.6 in MeCN [60]) did not reveal any catalytic activity due to triethylammonium being a weaker acid (Figure S2, supplementary information). Catalysts **1[−]** and **2[−]** exhibit similar behavior in the presence of TFA. The catalytic wave occurs at potentials more negative than those required for the reduction of the monoanionic complex to the dianion. Upon addition of acid, the reversibility of the redox couple for the complex is also lost. A concomitant shift of the reduction wave towards less negative potential values as the concentration of acid increases is also observed. All together, these data suggest that the dianionic form rapidly reacts with proton to form a novel catalytically active species. For catalyst **1[−]**, when the acid concentration reaches 5 mM, two distinct processes can be observed, with half-wave potentials of −1.42 and −1.68 V vs Fc^{+/0} (Figure 2). The

equilibrium reduction potential for TFA in MeCN into protons (5 mM) is calculated to be $-0.83\text{ V vs Fc}^{+/0}$ using the method described in the literature [9,60]. The overpotential requirements for these processes have been calculated as 0.587 V and 0.907 V , respectively (supplementary information, equation S1, Figure S3). By contrast, catalyst **2**⁻ exhibits only the first of these waves with a half-wave potential of $-1.3\text{ V vs Fc}^{+/0}$, corresponding to an overpotential requirement of 0.467 V (Figure 3).

In the case of catalyst **3**⁻ (Figure 4), the catalytic wave appears at potential values close to the potential required for the reduction of the complex to the trianion, with a mid-wave potential value of $-1.40\text{ V vs Fc}^{+/0}$ when the acid concentration is 5 mM . The reversibility of the **3**^{-/2-} couple is maintained and no shift of the anodic wave to less negative potential values is observed. This behavior is in contrast to that of catalysts **1**⁻ and **2**⁻. The overpotential requirement for this process is 0.567 V .

Hydrogen evolution measurements were performed in MeCN using a controlled-potential bulk-electrolysis setup with a glassy carbon rod electrode in MeCN for a 3 h period at a potential of $-1.2\text{ V vs Fc}^{+/0}$ for all complexes. The evolved hydrogen was quantified by gas chromatography. Catalyst **2**⁻ performs best, with TON of 158, compared to TON of 113 and 6 for catalysts **1**⁻ and **3**⁻, respectively. Faradaic yield was 71% for **1**⁻, 88% for **2**⁻, and 34% for **3**⁻ (Table 2).

The shift of the reduction potential towards less negative values that is observed for catalysts **1**⁻ and **2**⁻ as the concentration of TFA increases can be interpreted as the consequence of either an EC or a CE mechanism (with E denoting an electron transfer step and C indicating a chemical reaction - here protonation). In the first case, protonation is triggered by reduction while in the latter, the complex is protonated first. To investigate this process, a solution of each catalyst (0.1 mM) in deaerated MeCN was monitored with absorption spectroscopy in the presence of a large excess of TFA (50 mM , Figure 5).

The band at 866 nm in the presence of acid exhibits a hypochromic shift as a function of time. The presence of isosbestic points (inset, Figure 5) indicates the formation of one new species which absorbs at similar wavelengths, with a more pronounced shoulder at 800 nm compared to the spectrum without acid. Such a behavior indicates the slow formation of a protonated species. Since this band has been assigned to an intra-valence charge-transfer (IVCT) transition involving the radical anionic ligand: $[(L\bullet)M(L)] \leftrightarrow [(L)M(L\bullet)]$ [61], we propose that protonation occurs at sulfur. This procedure is partial reversed when a base soluble in MeCN is added (e.g trimethylamine, Figure S4). Formation of protonated species is therefore possible, although such a process is extremely slow by comparison to the cyclic voltammetry timescale. We therefore conclude that formation of **1H**⁻ and **2H**⁻ proceed through EC mechanisms.

Computational investigation of the hydrogen evolution mechanism

DFT calculations were employed to investigate the reaction intermediates and reaction pathways for catalysts **1**⁻ – **3**⁻.

The proposed mechanism for hydrogen evolution with catalyst **1**⁻ is shown in Scheme 2.

As shown in Scheme 2, catalyst $\mathbf{1}^{\bullet}$ is first reduced to the dianion and then protonation occurs in an exergonic step ($-38 \text{ kJ}\cdot\text{mol}^{-1}$). Protonation at sulfur to form $[\mathbf{1}(\text{SH})]^-$ is more favorable than protonation at nickel (forming $[\mathbf{1}(\text{NiH})]^-$) by $66 \text{ kJ}\cdot\text{mol}^{-1}$. Direct protonation of $\mathbf{1}^{\bullet}$ is found slightly endergonic ($16 \text{ kJ}\cdot\text{mol}^{-1}$) to yield $[\mathbf{1}(\text{SH})]$ which is more stable than $[\mathbf{1}(\text{NiH})]$ by $91 \text{ kJ}\cdot\text{mol}^{-1}$. $[\mathbf{1}(\text{SH})]$ can then be reduced to $[\mathbf{1}(\text{SH})]^-$ with a potential of -0.06 V vs $\text{Fc}^{+/0}$. In the next step, $[\mathbf{1}(\text{SH})]^-$ reduces to $[\mathbf{1}(\text{SH})]^{2-}$ with a calculated potential of -1.8 V vs $\text{Fc}^{+/0}$. $[\mathbf{1}(\text{NiH})]^{2-}$ is also observed with a similar stability as $[\mathbf{1}(\text{SH})]^{2-}$ within $3 \text{ kJ}\cdot\text{mol}^{-1}$. Another protonation ($-68 \text{ kJ}\cdot\text{mol}^{-1}$) leads to $[\mathbf{1}(\text{SH-SH})]^-$ which is only observed when protons are on distinct ligands. $[\mathbf{1}(\text{SH-SH})]^-$ can also be reached by protonation of $[\mathbf{1}(\text{SH})]^-$ ($-7 \text{ kJ}\cdot\text{mol}^{-1}$) to yield $[\mathbf{1}(\text{SH-SH})]$ and subsequent reduction (-1.16 V vs $\text{Fc}^{+/0}$). From $[\mathbf{1}(\text{SH-SH})]^-$, hydrogen is evolved in an exergonic reaction ($-110 \text{ kJ}\cdot\text{mol}^{-1}$) to yield the monoanionic catalyst $\mathbf{1}^{\bullet}$. Hydrogen evolution from $[\mathbf{1}(\text{SH-SH})]$ is calculated to be slightly endergonic ($16 \text{ kJ}\cdot\text{mol}^{-1}$). Despite this, the process is likely to be entropically driven due to the evolution of the dissociated H_2 molecule as a gas - an effect that is not adequately taken into account in the thermodynamic computation.

Catalyst $\mathbf{2}^{\bullet}$ follows a similar pathway for the hydrogen evolution reaction, with similar intermediates, protonation enthalpies, and redox potentials, as shown in Scheme 2. The entity $\mathbf{2}^{2-}$ can be protonated in an exergonic process ($-41 \text{ kJ}\cdot\text{mol}^{-1}$) to yield $[\mathbf{2}(\text{SH})]^-$ which is more stable than $[\mathbf{2}(\text{NiH})]^-$ by $76 \text{ kJ}\cdot\text{mol}^{-1}$. Further reduction of $[\mathbf{2}(\text{SH})]^-$ (-1.8 V vs $\text{Fc}^{+/0}$) yields $[\mathbf{2}(\text{SH})]^{2-}$ which is favored compared to $[\mathbf{2}(\text{NiH})]^{2-}$ by $12 \text{ kJ}\cdot\text{mol}^{-1}$. Alternatively, direct protonation of $[\mathbf{2}(\text{SH})]^-$ ($2 \text{ kJ}\cdot\text{mol}^{-1}$) yields $[\mathbf{2}(\text{SH-SH})]$ which is then reduced to give $[\mathbf{2}(\text{SH-SH})]^-$. On the other hand, an exothermic protonation of $[\mathbf{2}(\text{SH})]^{2-}$ ($-62 \text{ kJ}\cdot\text{mol}^{-1}$) leads to the doubly-sulfur protonated intermediate $[\mathbf{2}(\text{SH-SH})]^-$ that is more stable than $[\mathbf{2}(\text{NiH-SH})]^-$ by only $6 \text{ kJ}\cdot\text{mol}^{-1}$, indicating that participation of nickel ion in this step cannot be excluded. Finally, in a highly exergonic reaction ($-130 \text{ kJ}\cdot\text{mol}^{-1}$) hydrogen is evolved and monoanionic $\mathbf{2}^{\bullet}$ is formed.

The structures of the calculated intermediates are shown in Figure 6. The calculated structures for the monoanionic and dianionic states of $\mathbf{2}^{\bullet}$ in MeCN are in agreement with those experimentally reported in the literature [62–64], with calculated bond lengths within $0.04 \text{ \AA}$ of the experimental values (Table S2). The calculated value for the Ni hinge angle for $\mathbf{2}^{\bullet}$ differs significantly from the experimental value of 0° , but for the dianionic compound the calculated value of 0° is in agreement with the experimental value. Calculated structural parameters for compound $\mathbf{2}^{\bullet}$, its dianion and all calculated intermediates are summarized in Table 3 with the numbering scheme applied shown in Scheme 3.

Protonation of the dianionic catalyst (i.e. $[\mathbf{2}]^{2-}$) at S1 leads to a small tetrahedral distortion which is reflected in the value of the Ni hinge angle (5.2°) and an elongation of the C1 – S1 bond by $0.026 \text{ \AA}$ for $[\mathbf{2}(\text{SH})]^-$. Further reduction yields $[\mathbf{2}(\text{SH})]^{2-}$ which exhibits an even more distorted structure with a hinge angle of 27.1° and elongated Ni – S bonds, with Ni – S1 being the longest ($2.436 \text{ \AA}$). In the alternate route where $[\mathbf{2}(\text{SH})]^-$ is protonated prior to reduction, the distortion diminishes and a hinge angle of 2.4° is reached with minor elongation of the Ni – S1 bond. However, when the doubly-protonated and reduced state $[\mathbf{2}(\text{SH-SH})]^-$ is achieved, a high degree of distortion is observed (37.9°) with a concomitant

elongation of the Ni – S bonds; C – S bonds also appear longer, ca. 1.8 Å for C1 – S1, C4 – S4 and 1.77 Å for the remaining C – S bonds. For the calculated structure of intermediate $[2(\text{NiH})]^{2-}$ see Figure S5 and Table S1, supplementary information.

Further theoretical investigation of the hydrogen-evolving step reveals an intramolecular reaction pathway that involves one intermediate and two transition states (TS). We did not consider intermolecular schemes, such as those involving acid, as these would require supplementary theoretical approaches that are beyond the scope of this study. Scheme 4 depicts the intramolecular reaction profile in the case of 2^- . Very similar structures and energies are calculated for compound 1^- within experimental errors.

Starting from $[2(\text{SH-SH})]^-$ as the reactant (Ni hinge angle 42.7°), the first transition state (TS1) is reached which is located $26.3 \text{ kJ}\cdot\text{mol}^{-1}$ uphill and is more distorted with a hinge angle of 77.8° . At the same time, a H atom migrates from a sulfur atom to the nickel ion leading to a Ni-H bond to yield an intermediate with a slightly relaxed 76° hinge angle and S-H and Ni-H bond lengths of 1.35 Å and 1.46 Å, respectively. The proton and the hydride are within 3.044 Å, significantly closer than in $[2(\text{SH-SH})]^-$ (3.136 Å). Migration of the second proton to the nickel ion results in the formation of the second transition state (TS2), with an activation energy of $56.3 \text{ kJ}\cdot\text{mol}^{-1}$. In TS2, the hinge angle increases to 77.5° and both Ni-H bonds are significantly longer than the nickel-hydride distance in the intermediate ($\sim 1.65 \text{ Å}$ vs $\sim 1.46 \text{ Å}$), in line with the formation of a coordinated H_2 molecule with 0.831 Å H-H distance. From TS2, the reaction proceeds downhill to yield dihydrogen and the monoanionic catalyst 2^- .

Compound 3^- is the least active catalyst in the series but the calculated intermediates resemble those of catalysts 1^- and 2^- (Scheme 5). More specifically, protonation at sulfur occurs when 3^- has been reduced to the dianion. This is a slightly endergonic process ($14 \text{ kJ}\cdot\text{mol}^{-1}$) and yields the intermediate $[3(\text{SH})]^-$. Protonation at nickel produces the less stable (by $73 \text{ kJ}\cdot\text{mol}^{-1}$) species $[3(\text{NiH})]^-$ and is not favorable. Protonation at sulfur of the monoanionic state is strongly unfavorable ($101 \text{ kJ}\cdot\text{mol}^{-1}$), $[3(\text{SH})]^-$ can be reduced (-1.0 V vs $\text{Fc}^{+/0}$) to yield $[3(\text{SH})]^{2-}$ which is more stable than the nickel-protonated species $[3(\text{NiH})]^{2-}$ by $22 \text{ kJ}\cdot\text{mol}^{-1}$. Further protonation in an exergonic reaction ($-10 \text{ kJ}\cdot\text{mol}^{-1}$) yields $[3(\text{SH-SH})]^-$ which is more stable than $[3(\text{NiH-SH})]^-$ by $21 \text{ kJ}\cdot\text{mol}^{-1}$. From the $[3(\text{SH-SH})]^-$ state, hydrogen can evolve in an exothermic process ($-97 \text{ kJ}\cdot\text{mol}^{-1}$). For this compound, theoretical data suggest that protonation can also occur on the nitrogen atoms of the dithiolene ligands. This can be explained in terms of the electron-withdrawing effect of the mnt^{2-} ligand, in which the $-\text{CN}$ groups strip the sulfur atoms of electron density. Thus, the species $[3(\text{SH})]$ is more stable by $5 \text{ kJ}\cdot\text{mol}^{-1}$ compared to the $[3(\text{NH})]$ species. Further reduction yields the respective single-reduced species, with the sulfur-protonated $[3(\text{SH})]^-$ being more stable than $[3(\text{NH})]^-$ by $51 \text{ kJ}\cdot\text{mol}^{-1}$. When the double-reduced species are reached, $[3(\text{SH})]^{2-}$ and $[3(\text{NH})]^{2-}$, the sulfur-protonated species is more stable by $15 \text{ kJ}\cdot\text{mol}^{-1}$. In general, although protonation at nitrogen is plausible for this complex, the sulfur-protonated intermediate is calculated to be more stable.

On the decomposition of catalysts

The linear dependence of i_{cat} on the square root of the scan rate ($v^{1/2}$) indicates a diffusion-controlled homogeneous process [65] (Figure 8 and inset for catalyst **1**[•], Figure S6 for catalyst **2**[•]). To confirm this point, we performed three rinse tests for catalyst **1**[•] (Figure 7), in the same manner as reported earlier for Ni-bis(aryldithiolene) catalysts [53]. Initially the electrode was rinsed after a cyclic voltammetry scan and the electrode was transferred to a fresh solution of acid. Then, a cyclic voltammogram was recorded starting at a negative potential (-0.7 V vs Fc⁺⁰) to avoid oxidative redissolution of any deposited material. Almost no catalytic current was observed. Second, a linear sweep voltammogram of the catalyst in the presence of TFA was measured. This procedure was used to definitively exclude oxidative redissolution of any deposit during the reverse scan. However, subsequent CV measurement starting from -0.7 V vs Fc⁺⁰ did not show any catalytic behavior distinct from the pristine electrode. As a last conditioning method, a potential of -1.3 V vs Fc⁺⁰ was applied for 3 min, with a subsequent measurement of a cyclic voltammogram starting from -0.7 V vs Fc⁺⁰. Again, no catalysis was observed, indicating that catalysis under these conditions is of a homogeneous nature. The same was observed for catalyst **2**[•].

Discussion

Calculations confirm a kinetic preference for the monoprotonated monoreduced intermediate to be produced through a sequential downhill EC route, rather than from a CE pathway. The calculated enthalpies for the protonation of **1**[•] and **2**[•] are slightly endergonic (16 kJ·mol⁻¹ and 24 kJ·mol⁻¹, respectively) in line with the slow rate of protonation observed in the presence of excess of acid. Reduction potentials for [**1**(SH)] and [**2**(SH)] are calculated to be -0.06 V and 0 V vs Fc⁺⁰, respectively. Such positive values can however drive the CE pathway forward, especially as the concentration of acid increases.

In addition, catalysts **1**[•] and **2**[•] have similar calculated routes for hydrogen evolution and these two pathways nicely correspond to the two catalytic processes identified experimentally in Figures 1 and 2. H₂ evolution occurring in the first process therefore likely results from a double protonation of the dianionic species, followed by reduction of this deprotonated monoreduced species. This process can thus be described as an ECCE sequence. The second catalytic process goes through the reduction of the monoprotonated derivative of the monoreduced species and occurs at a more negative potential. Experimentally, catalysts **1**[•] and **2**[•] display distinct electrocatalytic behaviors in their cyclic voltammograms. Catalyst **2**[•] exhibits only one catalytic wave while **1**[•] shows two waves with lower catalytic peak currents. Such differences indicate that catalysis in the first process is slower for **1**[•] compared to **2**[•]. As a consequence, one might expect that the diffusion-reaction layer at the surface of the electrode is not fully depleted in protons at the top of the first wave so that there is still some substrate available for the second process occurring at the more negative potential. By contrast, fast catalysis by **2**[•] completely consumes protons so that none are left to be reduced in the second process.

Based on the calculated thermodynamic values, only one pathway towards hydrogen evolution is feasible for complex **3**⁻. This supports the observation of only one catalytic wave at the cyclic voltammogram of **3**⁻ in the presence of acid (Figure 4).

What becomes clear from the above observations is that protonation at sulfur induces elongation of the respective C – S and Ni – S bonds, along with the significant geometrical distortions that reduction imposes on the catalyst. This is in accordance with what was previously reported [58]. The dithiolene complexes under study are almost planar but their geometries seem to distort significantly during proton reduction as indicated by both experimental and theoretical data from this and previous work from our team [58]. Actually, variation in the Ni hinge angle seems to be of importance since reduced intermediates and transition states that eventually lead to the evolution of hydrogen exhibit tetrahedral distortion. The significant elongation of Ni – S bonds for the reduced protonated species [2(SH-SH)]²⁻ and [2(SH-SH)]⁻ reveals that each proton added affects the electronic structure of the ligand framework. More specifically, the delocalized nature of dithiolate ligands is altered and the Ni – S bonds acquire a bonding nature resembling that of Ni – S_{thiolate} analogs. This is reflected in bond lengths, since the calculated Ni – S bonds for **2**⁻ (2.325 – 2.436 Å) are close to those of similar [Ni(SPh)₄]²⁻ species reported in the literature (2.293 – 2.331 Å) [66].

We have been able to locate a pathway for intramolecular proton – hydride coupling that leads to the formation of a metal-bound H₂ molecule. The activation energy of this process was calculated to be ~60 kJ·mol⁻¹, a value that is in agreement with studies of similar H₂-evolving catalysts [27, 67–69] and enzymes [70]. As H₂ elimination is entropically favored, it is likely that the metastable H₂-bound molecule is not a true intermediate in the catalytic mechanism. In addition, we cannot exclude competition with direct intermolecular hydride-proton coupling involving a proton donor from the bulk (e.g., TFA). Accurate modelling of such a process requires more elaborate methods, such as hybrid quantum chemical/molecular mechanical (QC/MM) approaches that are beyond the scope of the current particular study. [71]

Significant attention has been drawn to whether electrocatalysis in organic solvents is of homogeneous or heterogeneous nature. More specifically, several studies on similar dithiolene- or thiolate-containing systems have shown that under reductive conditions a molecular catalyst may decompose to form a material which deposits on the surface of the electrode and is responsible for catalytic performance [27,44,54,72–75]. Several diagnostic criteria have been used to identify if a process is truly catalytic, most notably rinse tests in which the electrode, after a scan or a potential has been applied for a period of time, is transferred to a fresh solution containing only the acid. The rinse test experiments performed for catalysts **1**⁻ and **2**⁻ clearly support homogeneous/molecular H₂ evolution catalysis. Recently, Fang et al. in a meticulous study [54] reported on the processes that take place when **1**⁻ is employed as electrocatalyst in the presence of 4-bromo-anilinium tetrafluoroborate (pK_a = 9.43 in MeCN, *ibid.*). We were able to reproduce their findings (see Figure S7, supplementary information) with minor differences due to instrumentation and experimental conditions. Based on the different strength (3.27 pK_a units) of the acids used (TFA by us and 4-bromoanilinium by Fang et al.) we propose that even though under

reductive conditions and in the presence of acid catalyst **1**⁺ decomposes as shown by Fang et al., the degree of decomposition relies on the strength of the acid, with stronger acids leading to an extended degree of catalyst decomposition.

In this context, we examined the behavior of the cobalt analog of **1**⁺, [Co(bdt)₂](NBu₄) that has been reported as a catalyst for the reduction of protons by the groups of Eisenberg and Holland [43,44]. When investigated in a MeCN – water 1-1 mixture under anaerobic conditions in the presence of tosic acid (0.2 mM [Co(bdt)₂](NBu₄), 65 mM tosic acid), decomposition occurs. This can be seen from the absorption spectrum (see Figure S8, supplementary information), in which there is a decrease in absorbance with a concomitant increase in baseline, and a grey-black precipitate is formed (see Figure S8, supplementary information). This can be rationalized in terms of the increased acidity of tosic acid in mixed MeCN – water mixtures [76,77] which leads to degradation of the dithiolene complex.

Based on the above experimental findings on the dependence of acid strength, together with those for similar systems in the literature [39], and the calculated elongated Ni – S and C – S bonds of the reduced protonated species (see Table 3), we propose that decomposition of nickel bis-dithiolene complexes is dependent on the strength of acid employed, on the potential applied and most probably takes place via cleavage of Ni – S or C – S bonds when distorted geometries necessary for hydrogen evolution are reached.

4 Conclusions

In this paper we have investigated both experimentally and theoretically the hydrogen evolving mechanisms of a series of substituted dithiolene nickel complexes. We provide further support for the notion that substituents with electron donating ability on dithiolene rings improve the catalytic activity of the corresponding complexes towards proton reduction, whereas strong electron donating substituents like-CN significantly reduce this activity. The mechanisms proposed include reduction of the catalyst to the dianion, protonation at sulfur and subsequent protonation and reduction (main route for complex **2**⁻) or reduction and then protonation (main route for complex **1**⁺), both leading to abstraction of hydrogen in an exergonic process that regenerates the monoanionic catalyst.

Theoretical data indicate that during the proton reduction process intermediates adopt a tetrahedral configuration with the hinge angle between S1-Ni-S2 and S3-Ni-S4 planes playing a prominent role in hydrogen evolution. Moreover, the asymmetric substitution of the dithiolene ligands with electron donating groups further support this structural distortion, as witnessed by the higher activity of catalyst **2**⁻. Finally, calculations suggest that a sulfur-protonated Ni-hydride intermediate cannot be excluded.

In addition, experimental data indicate that decomposition of metal bis-dithiolene complexes is dependent on the strength of acid employed, on the potential applied, and most probably takes place via cleavage of M – S or C – S bonds in the distorted geometries that are necessary for hydrogen evolution. However, for medium strength acids, the catalytic activity of this class of compounds appears to be homogeneous.

This study supports our previous findings that dithiolene complexes with more rigid structure and less charge delocalization over the NiS₄ core are better reductive catalysts than those that have appeared up to now in the literature. As a result of this, we are currently pursuing the design and synthesis of more efficient dithiolene-based catalysts.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Normalized cyclic voltammograms for compounds **1**⁺, **2**⁺, and **3**⁺ in MeCN at a scan rate of 100 mV s⁻¹ with TBAPF₆ in MeCN under Ar at room temperature. Glassy carbon working electrode, Ag/AgCl reference electrode, platinum wire counter-electrode.

Figure 2.

Cyclic voltammogram of 1^+ (1 mM) in the presence of increasing equivalents of trifluoroacetic acid: no acid, green; 1 eq, light blue; 3 eq, yellow; 5 eq, red; 10 eq, dark blue. Glassy carbon working electrode, Ag/AgCl reference electrode, platinum wire counter-electrode, scan rate 100 mV s⁻¹ with TBAPF₆ in MeCN as supporting electrolyte.

Figure 3.

Cyclic voltammogram of 2^+ (1 mM) in the presence of increasing equivalents of trifluoroacetic acid: no acid, green; 1 eq, light blue; 3 eq, yellow; 5 eq, red; 10 eq, dark blue. Glassy carbon working electrode, Ag/AgCl reference electrode, platinum wire counter-electrode, scan rate 100 mV s⁻¹ with TBAPF₆ in MeCN as supporting electrolyte.

Figure 4.

Cyclic voltammogram of 3^+ (1 mM) in the presence of increasing equivalents of trifluoroacetic acid: no acid, green; 1 eq, light blue; 3 eq, yellow; 5 eq, red; 10 eq, dark blue. Glassy carbon working electrode, Ag/AgCl reference electrode, platinum wire counter-electrode, scan rate 100 mV s⁻¹ with TBAPF₆ in MeCN as supporting electrolyte.

Figure 5. UV-Vis spectrum of catalyst 1^+ (0.1 mM) in the presence of 50 mM TFA. Spectra were recorded in deaerated MeCN at 15 min intervals.

Figure 6.

Calculated structures for intermediates in the proposed hydrogen evolution mechanism of compound 2^- .

Figure 7.

Rinse tests for catalyst **1**⁺ (glassy carbon working electrode). Cyclic voltammogram for catalyst **1**⁺ in the absence (grey dotted trace) and presence (black trace) of 10 mM TFA in MeCN. Each trace indicates scan of a rinsed working electrode in a fresh solution of 10 mM TFA in MeCN. Red trace: after measurement of a cyclic voltammogram; green trace: after a linear sweep voltammogram; blue trace: after a potential of -1.3V applied for 3 min.

Figure 8.

Cyclic voltammogram of catalyst **1*** in the presence of 10 mM TFA at various scan rates.

Inset: linear dependence of $i_{\text{cat.}}$ on $v^{1/2}$ ($R^2=0.98$, glassy carbon working electrode)

Scheme 1.

Catalysts **1⁻**, **2⁻**, and **3⁻**. Tetra-n-butylammonium counter-cation is omitted for clarity.

Scheme 2.

Proposed hydrogen evolution mechanism for catalysts **1⁻** and **2⁻**, along with protonation enthalpies and reduction potentials. Potentials are reported vs $\text{Fc}^{+/0}$.

Scheme 3.
Numbering scheme for catalyst 2⁻.

Scheme 4.

Calculated reaction pathway for the hydrogen-evolving step of the mechanism in Scheme 2 with catalyst **2**⁻. TS denotes transition state, numbers in parentheses indicate calculated energy values (kJ·mol⁻¹) and values of the Ni hinge angle (degrees). Significant bond lengths are indicated with arrows.

Scheme 5.

Proposed hydrogen evolution mechanism for catalyst 3^- , along with protonation enthalpies and reduction potentials. Potentials are reported vs $\text{Fc}^{+/0}$.

Table 1 Redox potentials for complexes **1**^{•-}, **2**^{•-}, and **3**^{•-}.

Compound	<i>E</i> vs Fc ^{+/0}	
	monoanion/dianion	dianion/trianion
1 ^{•-}	-0.92	-
2 ^{•-}	-0.95	-
3 ^{•-}	-0.08	-2.00

Table 2

Bulk electrolysis results for complexes **1**⁺, **2**⁺, and **3**⁺ in MeCN in the presence of 50 mM trifluoroacetic acid.

Compound	TON	Faradaic yield ^a
1 ⁺	113	0.71
2 ⁺	158	0.88
3 ⁺	6	0.34

^a bulk electrolysis was performed at – 1.2V vs Fc^{+/0} for a 3 h period, catalyst concentration 0.1 mM

Table 3

Selected structural parameters calculated for intermediates in the hydrogen evolution mechanism of catalyst **2**⁻.

Parameter ^a	[2] ⁻	[2] ²⁻	[2(S-H)] ⁻	[2(S-H)] ²⁻	[2(SH-SH)]	[2(SH-SH)] ⁻
Ni – S1	2.193	2.229	2.255	2.436	2.260	2.353
Ni – S2	2.198	2.234	2.234	2.371	2.208	2.325
Ni – S3	2.199	2.229	2.199	2.325	2.211	2.347
Ni – S4	2.197	2.234	2.222	2.336	2.253	2.363
C1 – S1	1.758	1.776	1.802	1.802	1.797	1.801
C2 – S2	1.758	1.775	1.768	1.762	1.772	1.769
C3 – S3	1.760	1.775	1.774	1.777	1.773	1.773
C4 – S4	1.758	1.775	1.777	1.777	1.801	1.803
S1 – H1	-	-	1.351	1.352	1.353	1.351
S4 – H2	-	-	-	-	1.352	1.350
Ni hinge angle	7.5°	0.8°	5.2°	27.1°	2.4°	37.9°

^a numbering scheme is the same as Scheme 3 with protonation at S1 and S4. Bond lengths are given in Å.

The Ni hinge angle is the angle between the Ni-S1-S2 and Ni-S3-S4 planes.