Inept N\(_2\) Activation of Tri-Nuclear Nickel Complex with Labile Sulfur Ligands Facilitates Selective N\(_2\)H\(_4\) Formation in Electrocatalytic Conversion of N\(_2\)

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Abstract: Conversion of N\(_2\) to the energy vector N\(_2\)H\(_4\) under benign conditions is highly desirable. However, such N\(_2\) fixation processes are extremely rare. It has been recently reported that N\(_2\) to N\(_2\)H\(_4\) conversion can be achieved electrochemically by using a trinuclear [Ni\(_3\)(S\(_2\)C\(_6\)H\(_5\))\(_3\)]\(^2\) complex (named as [Ni\(_3\)S\(_8\)]\(^2\)). There are hardly any precedents of Nitrogen Reduction Reaction (NRR) by molecular catalysts having Ni and the highly unusual selectivity for N\(_2\)H\(_4\) over NH\(_3\) makes this electrochemical reduction unique. A systematic theoretical study employing calibrated Density Functional Techniques to unearth the mechanisms of NRR (4e/4H\(^+\)) and HER (2e/2H\(^+\)) was conducted for the aforementioned trinuclear Ni complex. Our findings unravel a curious case of ligand lability working in tandem with metal centers in facilitating this unprecedented electrocatalytic activity. Furthermore, it is shown that the poor N-N bond activation property of Ni is responsible for this unusual selectivity. Additionally, the HER mechanistic pathways have also been delineated in this report. The mechanistic intricacies thus unearthed in this study may assist in developing more efficient electrocatalysts for N\(_2\)H\(_4\) production through NRR.

Introduction: The artificial fixation of nitrogen by Haber and Bosch had ushered in sustenance of the ever-increasing population by facilitating production of NH\(_3\) as a chemical feedstock for fertilizer synthesis from aerial N\(_2\)[1]. Although it is hailed as one of the greatest discoveries of mankind, over the past few decades researchers had invested their efforts to unearth more benign routes through solar, electrochemical for N\(_2\) conversion to NH\(_3\) [2] as the commercial production of NH\(_3\) is associated with significant carbon footprint[3]. The inertness of N\(_2\) poses an unassailable challenge to its fixation regardless of the fact that N\(_2\) conversion to NH\(_3\) is a thermodynamically feasible process (\(\Delta G^\circ\) (298 K) of NH\(_3\) (from N\(_2\) and H\(_2\)) is -16.4 kJ/mol). A significantly more daunting task is the conversion of N\(_2\) to N\(_2\)H\(_4\) which is also thermodynamically uphill (\(\Delta G^\circ\) (298 K) of N\(_2\)H\(_4\) (from N\(_2\) and H\(_2\)) is +159.2 kJ/mol) along with the kinetic challenge associated with N\(_2\) activation process [4]. N\(_2\)H\(_4\) can serve as an important energy vector [5]. Moreover, if it can be produced in a carbon neutral path may make chemical hydrogen storage feasible and sustainable [6]. Current industrial methods for producing N\(_2\)H\(_4\) indirectly depend upon the Haber–Bosch process which produces NH\(_3\) feedstocks. Thus commercial N\(_2\)H\(_4\) production is associated with a significant carbon footprint. In nature, the conversion of N\(_2\) to NH\(_3\) is achieved under ambient conditions by the nitrogenase enzyme[7,8]. The nitrogenase model of N\(_2\) fixation has been thoroughly investigated and had inspired the development of several catalysts [9-14]. Unfortunately, most of these catalysts use sacrificial reductants. Of late the focus has shifted to achieve this singularly important transformation electrochemically as electricity produced from carbon neutral sources such as wind, solar or hydro will render it sustainable in the long run [15]. Electrochemical N\(_2\) fixation has emerged as an alternative which holds the promise of achieving transformation of N\(_2\) to NH\(_3\) under mild conditions [16-18].

Instances of Nitrogen fixation yielding N\(_2\)H\(_4\) as the major product as opposed to NH\(_3\) are scarce. Many NRR (Nitrogen Reduction Reaction) molecular catalysts form N\(_2\)H\(_4\) as a side product, out of which Fe complex by Ashley et al. was the first to reverse the trend, forming N\(_2\)H\(_4\);NH\(_3\) in the ratio of 24:1 [19]. Of late a remarkable finding was reported by Dey and co-workers wherein they have developed the first molecular complex [Ni\(_3\)S\(_8\)]\(^2\) which reduces N\(_2\) to N\(_2\)H\(_4\) as the only nitrogenous product electrochemically [20].

\[
\text{N}_2 + \text{PhOH} \quad \xrightarrow{\text{Cat. } [\text{Ni}_3\text{S}_8]^2} \quad \text{N}_2\text{H}_4 + \text{H}_2
\]

\((\text{proton donor})\)

\((\text{THF, rt})\)

Scheme 1: Reaction studied in this work.

The intermediates involved in the catalytic mechanism have not been identified and the underlying mechanism was unclear from the reported experimental findings. Furthermore, there are hardly any precedents of NRR by Ni. The situation is complicated due to competing NRR and HER (Hydrogen evolution reaction) at similar reduction potentials [21]. Hence it presents a wonderful opportunity for theoretical comprehension of the mechanistic roadmap of this intriguing and unique
Results and Discussion:

a) Nitrogen Reduction Reaction:

Steps up to Nitrogen Binding: Initially the structure of [NiS8]2− was optimized and its affinity to bind N2 was checked. The di-anionic complex [NiS8]2− did not show any propensity to bind N2 at any of the central or terminal Nickel atoms [see Fig. S5]. This prompted us to investigate the chances of protonation at the bridging and terminal Sulfur which was found to be 26.7 and 10.6 kcal/mol endoergic respectively [see Fig. S6]. Hence, we propose that the complex is likely to undergo reduction first. Moving to case of initial reduction, the first reduction potential of bare [NiS8]2− was found to be too negative (E = -3.18 V; see Supplementary Information). Therefore, a water molecule was included in the model prior to reduction resulting in a structure which is isoenergetic to [NiS8]2−. This structure with one explicit water named as 3[A0.8]2− (see Scheme 2) starts our catalytic NRR cycle. The computed reduction potential of this intermediate turned out to be -2.68 V, which is a significant change after inclusion of a single explicit water molecule, indicating the importance of non-covalent interactions while calculating reduction potentials [30-31]. In order to test the validity of our reduction scheme, we tried to calculate the reduction potential of [NiS8]2− with three trapped water molecules inside the cage of the molecule as was reported in the XRD structure [20]. It resulted in a calculated redox potential of -2.54 V compared to experimental redox potential of -2.40 V in Ar/N2 (in the absence of proton donor PhOH) assigned to the central Ni atom [20]. The SOMO of [NiS8]2−.3H2O in Fig. 2 and spin density [see Fig. S2] shows the presence of unpaired electron at central Ni. The reduced complex [B1.0]2− is able to break a Ni-S bond to bind N2: This is in line with the findings of Kartik et al. where it was shown N2 could bind to Ni only after a single electron reduction [32].

B. Computational Details: All density functional calculations were conducted using the Gaussian09 package [26]. All molecular geometries were optimized in vacuum with B3LYP density functional [27] paired with 6-31++G (d,p) basis set for C, H, S, O, N and LanL2DZ, which has a double-ζ quality basis set with the Los Alamos effective core potential for Ni in room temperature. Each intermediate and transition state is characterized by all real frequencies and a single imaginary frequency, respectively. Single-point solvent phase calculations were carried out using B3LYP in the CPCM [28] solvent model for Tetrahydrofuran using the same basis set. For obtaining solvent-phase-corrected free energy, we included the standard entropic correction to the ideal gas phase model [29]. The free energies for the protonation steps were calculated against PhOH/PhO− pair. The methodologies used for obtaining calculated reduction potentials are described in supplementary information. The reduction potentials are reported in B3LYP density functional with LANL2DZ (Ni) and 6-31++G (d,p) (C, H, N, O, S) basis set in the main manuscript. The results with other density functionals and basis sets have been discussed in Table S1-S6.

Figure 1: Structure of the catalyst [Ni5(S2C4H10)4]2− abbreviated as [NiS8]2− with atom numbers labelling used in this work.

Figure 2: Singly occupied molecular orbital of [NiS8]2−.3H2O. Color code used : Green – Ni, Yellow – Sulfur, Black – C, Grey – H, Red – Oxygen.
The Ni-N bond length in $[^2]{[C_1,0]}^3$ was found to be 1.92 Å. Such a pseudo-tetrahedral coordination of N$_2$ with Ni in $[^2]{[C_1,0]}^3$ is rare and has been found earlier in some Nickel tri-phosphine complexes [33]. A favourable non-covalent interaction of PhOH with Sulfur atoms is also possible instead of H$_2$O prior to the first reduction, but this path leads to a more favourable HER pathway which has been discussed later in Scheme 3. The N$_2$ bond length in $[^2]{[C_1,0]}^3$ is 1.12 Å (slightly activated) and HOMO is shown in Figure 3a. Next, two consecutive protonations were performed using Phenol as the proton donor at S9 and S6 (see Figure 1 for atom labels) as reduction of $[^2]{[D_1,1]}^2$ was found to be too negative. Hence, two consecutive protonations were done on intermediate $[^2]{[C_1,0]}^2$ leading to the formation of $[^2]{[E_1,2]}^3$.

Steps after N$_2$ binding: The reduction of $[^2]{[E_1,2]}^3$ occurs at calculated $E = -2.69$ V to form $[^1]{[F_2,2]}^2$. $[^1]{[F_2,2]}^2$ shows an increase in N$_2$ bond length from 1.12 Å to 1.24 Å which is the first sign of N$_2$ activation. The HOMO of $[^1]{[F_2,2]}^2$ shows the electron donation from Sulfur atoms and d-orbitals of Ni to $\pi^*$ of N$_2$. The Ni-N bond decreases from 1.92 Å in $[^2]{[C_1,0]}^3$ to 1.74 Å in $[^1]{[F_2,2]}^2$. The NPA charges on N$_\alpha$ and N$_\beta$ were found to be -0.07|e| and -0.16|e| [see Table. S8].

Notably, the product for distal protonation, $[^1]{[H_2,2]}^2$ is stabilized by two hydrogen bond formation with S atoms. The N-N bond length in $[^1]{[H_2,2]}^2$ is 1.24 Å and the NPA charges were found to be -0.19|e| and -0.40|e| at N$_\alpha$ and N$_\beta$ respectively [see Table S8]. It was found that the distal product $[^1]{[H_2,2]}^2$ accepts an electron at $E = -2.36$ V which provides a surprisingly striking

Scheme 2: Mechanism for NRR. The indexing scheme for the intermediates is shown in the middle of the figure. Reaction free energies are reported in kcal/mol, reduction potentials are reported against Fc$^+/Fc^-$. Addition of H$^+$ here refers to protons extracted from phenol. Free energies for protonation at S ($\Delta G_p$) and activation energy barriers for proton transfer from S to N ($\Delta G_{pt}$) are shown in square bracket. The non-covalent interactions is shown by dashed grey lines. B3LYP functional with LANL2DZ (Ni) / 6-31++G(d,p) basis set was used for determining Gibbs free energies.
agreement with the experimental onset NRR catalytic response at $E = -2.35$ V. Next protonation at S9 stabilizes this charged intermediate $^2[1_{3,2}]^+$ by 23.6 kcal/mol. The final reduction at $E = -2.44$ V is energetically uphill by only 2 kcal/mol. The last two protonations of intermediates $^3[1_{3,2}]^+$ and $^1[K_{4,3}]^+$ are highly exergonic and provide a thermodynamic sink for the difficult hydrazine formation. $[L_{4,4}]^2$ has a Ni-N and N-N bond length of 1.98 Å and 1.46 Å respectively. $N_2H_4$ was formed at $[L_{4,4}]^2$ and the transition state for $N_2H_4$ release was found to be 10.9 kcal/mol with respect to $[L_{4,4}]^2$. In this transition state the dissociated Ni-S linkage is formed again with the simultaneous release of $N_2H_4$. It was interesting to note that the last three reductions were not much affected by an explicit water molecule.

We had also investigated the possibilities of further protonation on $N_6$ and $N_8$ deliberately to examine if this can lead to $N_3$ formation [see Fig. S8]. Generally, metals like Re, Mo form bimetallic complexes with $N_2$ resulting in a strong activation due to efficient metal to N backbonding leading to formation of stable metal nitrides [16, 35, 36]. The strong bonding between the metal and the proximal N atom in turn weakens the NN bond. Furthermore, as the lone pairs of the proximal N atoms are involved in the back-bonding they are less prone to protonation. This phenomenon essentially favors a distal pathway to release $N_3H$. In the instant case involving Ni$^{2+}$($d^8$) the back-bonding simply does not arise, thus leaving the proximal N atom’s lone pair free for protonation. Protonation at $N_6$ (to form [Ni-NH$_2$-NH$_3$]$^+$) in $[L_{4,4}]^2$ was exergonic by 4.0 kcal/mol and releases Hydrazinium ($N_2H_5^+$). Protonation at $N_8$ (to form [Ni-NH$_2$-NH$_3$]$^+$) was endoergic by 6.5 kcal/mol and did not lead to release of $N_2H_5^+$ or $NH_3$ [see Fig. S8]. Such [M-NH$_2$-NH$_3$]$^+$ structures have rarely been experimentally observed (or theoretically predicted) with other metals and can occur in rare case of weak late stage N-N cleavage. Szilvasi and co-workers [37] had theoretically studied the formation of [Fe]-NH$_3^+$ from a [Fe]-NH$_2$-NH$_2$ structure, in which [Fe]-NH$_2$-NH$_3^+$ could not be located in PES indicating spontaneous $NH_3$ release upon protonation and the [Fe]-NH$_2^+$ product was highly exergonic. However, in our case the activation barrier for $NH_3$ release was found to be steep 29.9 kcal/mol higher than that of the previous [Ni-NH$_2$-NH$_3$]$^+$ intermediate [see Fig. S8], which suggests that Ni has a poor $N_2$ activation power resulting in this highly unusual selectivity for $N_2H_4$ over $NH_3$. Overall, the initial energetically uphill steps of NRR cycle could be achieved in the presence of external electrochemical potential [38], while the exergonic reductive protonations in the later stage helps in driving the NRR process.

b) Hydrogen Evolution Reaction:

In Scheme 2 we have discussed about the importance of non-covalent interactions in calculating reduction potentials. For HER (see Scheme 3) we start with a similar non-covalent interaction of [NiH$_4$]$^2$ with the proton donor phenol and name the starting intermediate as $^1[a_{6,0}]^2$. This interaction of phenol is shown in $^1[b_{6,0}]^2$ which is favourable by 5.5 kcal/mol as compared to the starting intermediate $^1[a_{6,0}]^2$. $^1[b_{6,0}]^2$ has a calculated reduction potential of -2.64 V, which may be the reason behind rise of catalytic currents with increasing PhOH concentrations [20]. Reduction of $^2[d_{1,1}]^2$ at $E = -2.85$ V forms a Ni-hydride.
bond leaving a thiolate anion uncoordinated at a free energy cost of \( \Delta G = +11.6 \text{ kcal/mol} \). Protonating this thiolate back forms an intermediate \([f_{2,2}]^-\) which has proton and hydride in close vicinity leading to hydrogen evolution (major catalytic path). The T.S for HER has an activation energy barrier of 19.5 kcal/mol with respect to \([f_{2,2}]^-\). Alternatively, protonation of \([d_{1,1}]^-\) at S10 can occur at a cost of \( \Delta G = +11.2 \text{ kcal/mol} \). Reduction of the newly formed intermediate \([g_{1,2}]^-\) at \( E = -2.31 \text{ V} \) leads to a proton transfer from S10 to S11 (see Fig. 1 for atom labels) and a simultaneous Ni-H bond formation (by migration of proton initially at S9) during the course of geometry optimization. Formed intermediate \([h_{2,2}]^-\) cannot eliminate \( H_2 \) as the proton and hydride are far away (2.74 Å). \([h_{2,2}]^-\) has to undergo a rearrangement to \([f_{2,2}]^-\) by another proton transfer before finding the T.S for HER, which makes it a less favourable minor pathway. Thus, two pathways for HER were found, with reduction potential values -2.85 V and -2.31 V respectively. This feature has a strong resemblance with the experimentally found major catalytic response at -2.85 V and minor catalytic response at -2.35 V for HER [20]. This observation further confirms that our findings are in line with the experiment [20].

**Conclusion:** Our theoretical studies reveal that the lability of the thiolate ligands of the electrocatalytic \([Ni_3S_8]^2-\) complex in the presence of electrons and proton source enables it to bind \( N_2 \) and reduce it to \( N_2H_4 \). In particular \( \eta^3 \) sulfurs in dithiolate ligands belonging to the central metal in the trinuclear species are susceptible to cleavage on acceptance of an electron which vacates a coordination site on a terminal Ni to initiate \( N_2 \) fixation. Sequential protonations tactfully stabilize the \( \{N_xH_y\} \) intermediates along the electrocatalytic cycle. Contrary to previous suggestions, our theoretically predicted electro-reduction mechanism does not show any multi-metal coordination of \( N_2 \) or \( N_2 \) related intermediates for formation of \( N_2H_4 \). The activation energy barriers for the proton transfer from sulfur to nitrogen are found to be low. The catalyst proves to be very selective towards \( N_2H_4 \) over \( NH_3 \) as found by the activation energy barrier for \( N_2H_4 \) (10.9 kcal/mol) and \( NH_3 \) (29.9 kcal/mol) release and the ineptitude of \( Ni^{2+} \) in \( N_2 \) activation implicated for this observation. The HER mechanism is explained quite well with both major and minor pathways. Our model seems to predict the mechanism of an electrochemical reduction in a non-aqueous solvent with reasonable accuracy.
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