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## COMMUNICATION

## Electrocatalytic H<sub>2</sub> evolution promoted by a bioinspired (N2S2)Ni(II) complex

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We have investigated a bioinspired (N2S2)Ni(II) electrocatalyst that produces H<sub>2</sub> from CF<sub>3</sub>CO<sub>2</sub>H with a turnover frequency (TOF) of ~1,250 s<sup>-1</sup> at low acid concentration (<0.043 M) in MeCN. A mechanism for the H<sub>2</sub> production by this (N2S2)Ni(II) electrocatalyst is proposed and its activity is benchmarked against those of other reported molecular Ni H<sub>2</sub> evolution electrocatalysts. Importantly, the involvement of a hemilabile pyridyl group of the N2S2 ligand is proposed to mimic the role of a cysteine residue involved in the biological proton reduction performed by [NiFe] hydrogenases.

Hydrogen (H<sub>2</sub>) is a key ingredient for fuel cell technologies needed for the future use of renewable energy sources on a larger scale.<sup>1</sup> The primary challenge of such technologies is to implement earth-abundant materials to produce H<sub>2</sub> with high turnover frequency (TOF). In this area, biological catalysts such as [NiFe] hydrogenases that exhibit TOFs of ~1000 sec<sup>-1</sup> under weak acidic conditions have been the inspiration for reducing H<sup>+</sup> to H<sub>2</sub>.<sup>2</sup> The H<sup>+</sup> transfer events are controlled at the Ni center, which is bound to two terminal cysteine (Cys) groups and two bridging Cys thiolates. The terminal in the HER catalytic cycle is the Ni-R state that releases H<sub>2</sub> and returns to the resting state Ni-Sla (Fig. 1).<sup>3</sup>

Although structural mimics of [NiFe] hydrogenases have been reported, their performance in catalytic HER is either not described or kinetically sluggish.<sup>4</sup> Furthermore, there are other efficient mononuclear Ni complexes reported for electrocatalytic HER. For example, DuBois et al. reported Ni phosphine complexes that feature flexible amine arms as proton relay groups and perform HER using a strong acid, protonated dimethylformamide ([DMF-H]<sup>+</sup>, pK<sub>a</sub> = 6.1 in MeCN).<sup>5</sup> Later, DuBois et al. and Dempsey et al. investigated the

electrochemical HER mechanism of such Ni phosphine complexes and showed that the flexible second coordination sphere amine arms do not interact with the Ni center, yet they only shuttle protons through H-bonding.<sup>6</sup> However, a common drawback for these molecular HER electrocatalysts is the use of strong acids and often at high concentrations in non-aqueous electrolytes to achieve high turnover frequencies.

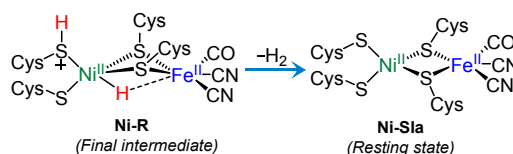


Fig. 1. The final step observed in [NiFe] hydrogenases catalyzed the HER cycle.

A few reported molecular Ni<sup>II</sup> electrocatalysts perform HER at low overpotential using weak acids. Jones and co-workers reported a S<sub>2</sub>P<sub>2</sub>-coordinated Ni HER electrocatalyst, which produces H<sub>2</sub> from CH<sub>3</sub>CO<sub>2</sub>H (AcOH, pK<sub>a</sub> = 22.48 in THF) at only 240 mV of overpotential, yet with a low TOF of 1,240 s<sup>-1</sup>.<sup>7</sup> In addition, a Ni complex bearing phosphinopyridyl ligands with amine residues as H<sup>+</sup> transfer sites showed comparatively higher TOF of 8,400 s<sup>-1</sup> using AcOH in MeCN (pK<sub>a</sub> = 23.51), but at a high overpotential (590 mV).<sup>8</sup>

Herein we report the synthesis and characterization of a bioinspired Ni complex [(N2S2)Ni<sup>II</sup>(MeCN)<sub>2</sub>](OTf)<sub>2</sub>, **1**·(OTf)<sub>2</sub>, where N2S2 is 3,7-dithia-1,5(2,6)-dipyridinacyclooctaphane (Fig. 2). We then studied the electrocatalytic HER reactivity of **1**<sup>2+</sup> in MeCN using the acids CF<sub>3</sub>CO<sub>2</sub>H (TFA, pK<sub>a</sub> = 12.65)<sup>9</sup> or AcOH as the proton sources. Remarkably, **1**<sup>2+</sup> showed HER electrocatalytic activity with a TOF of ~1,250 s<sup>-1</sup> using only 0.043 M of TFA in MeCN with ≤ 2 M H<sub>2</sub>O. We attribute such elevated performance of **1**<sup>2+</sup> at low acid concentrations to the role of one of the pyridyl group of N2S2 in proton binding and transfer events during HER. Our previous studies have shown that the N2S2 ligand is conformationally flexible and can adopt *k*<sup>2</sup>, *k*<sup>3</sup>, and *k*<sup>4</sup> binding modes depending on the geometric preference of the metal center.<sup>10</sup> Thus, the 'hemilabile' nature of the pyridyl group in N2S2 that can act as both a ligand and a proton

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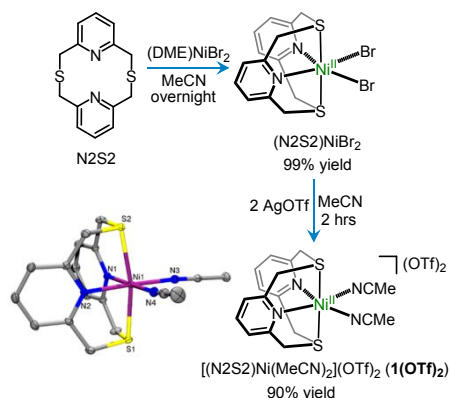
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relay can be viewed as mimicking the role of Cys residues in [NiFe] hydrogenases.<sup>11</sup>

The N2S2 ligand was prepared following a slightly modified literature procedure, and **1**·(OTf)<sub>2</sub> was synthesized as a purple solid in up to 90% yield.<sup>12</sup> Single crystal X-ray analysis of **1**·(OTf)<sub>2</sub> reveals a tetragonally distorted octahedral coordination of the Ni<sup>II</sup> center, with the two N atoms of the N2S2 ligand and two MeCN molecules occupying the equatorial positions, with an average Ni–N bond distance of 2.06 Å (Fig. 2). The two S atoms of N2S2 occupy the axial positions with comparatively longer average Ni–S bond lengths of 2.386 Å, thus completing a κ<sup>4</sup> binding mode for the N2S2 ligand.



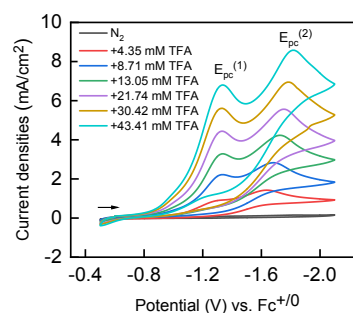
**Fig. 2.** Synthetic scheme for [(N2S2)Ni(MeCN)<sub>2</sub>](OTf)<sub>2</sub> (**1**·(OTf)<sub>2</sub>) and ORTEP representation (50% probability ellipsoids) for **1**<sup>2+</sup> (bottom left). Selected bond distances (Å): Ni1–N1 2.071(9), Ni1–N2 2.060(10), Ni1–S1 2.379(3), Ni1–S2 2.394(3), Ni1–N3 2.060(10), Ni1–N4 2.039(10).

We then studied the electrochemical behavior of **1**<sup>2+</sup> in N<sub>2</sub>-saturated 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (TBAP)/MeCN. The cyclic voltammograms (CVs) of **1**<sup>2+</sup> showed a quasi-reversible redox wave centered at –1.30 V vs. Fc<sup>+/0</sup> and an irreversible wave at –1.75 V vs. Fc<sup>+/0</sup>, assigned to the Ni<sup>II/I</sup> and Ni<sup>I/0</sup> redox couples, respectively (Fig. S5a).<sup>12</sup> Scan rate dependence CVs confirmed diffusion-controlled electrochemical processes by exhibiting a linear correlation between the cathodic peak currents at the Ni<sup>II/I</sup> reductive wave and the square root of the scan rates (Fig. S5b and S6).<sup>13</sup>

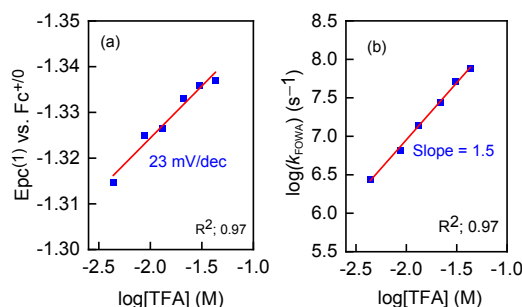
The electrochemical HER activity of **1**<sup>2+</sup> was first tested using AcOH as the acid. The addition of AcOH showed an increase in the peak current densities at potentials lower than –2 V (Fig. S7), yet the current enhancement for **1**<sup>2+</sup> overlapped with the background electrode contribution (Fig. S11). A stronger acid, TFA, was then chosen, and the CVs recorded for **1**<sup>2+</sup> in the presence of TFA exhibit catalytic current enhancement for two cathodic peak potentials, E<sub>pc</sub><sup>(1)</sup> and E<sub>pc</sub><sup>(2)</sup>, and the peak current densities increased as the concentration of TFA was increased up to 43.41 mM (Fig. 3). The onset potentials of these catalytic CVs were at least 500 mV more positive than the reduction potential of Ni<sup>II/I</sup>, E<sub>Ni(II/I)</sub>. Additionally, the catalytic peak potentials (E<sub>cat</sub>) were ≥ 365 mV more positive than that of GC-promoted HER in the absence of **1**<sup>2+</sup> (Fig. S12).

To investigate the mechanism of HER process catalyzed by **1**<sup>2+</sup>, the shift in E<sub>pc</sub><sup>(1)</sup> was plotted vs. log[TFA] and fitted linearly to yield a slope of 23 mV/dec (Fig. 4a, blue dots), indicating a

typical EC-type electrochemical mechanism, where E is the Nernstian e<sup>–</sup> transfer, followed by an irreversible chemical (C) step.<sup>13</sup> The catalytic peak currents did not plateau upon the further increase in TFA concentration (>0.043 M). Therefore the Randles-Sevcik equation cannot be applied to obtain the catalytic rate constant. Instead, foot-of-the-wave analysis (FOWA) was used to estimate the rate constants (k<sub>FOWA</sub>, Table S1) for the C step (the first protonation step) at different TFA concentrations by subtracting the background currents observed for the bare GC electrode under identical electrochemical conditions (Fig. S16).<sup>9</sup> The log(k<sub>FOWA</sub>) values were plotted vs. log[TFA] and a slope of 1.5 was obtained (Fig. 4b), suggesting the order of the reaction in acid is greater than 1.



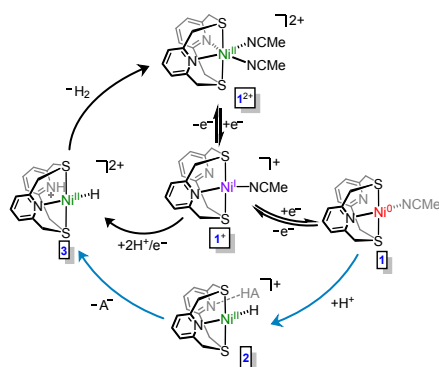
**Fig. 3.** CVs of **1**<sup>2+</sup> (1 mM) without (black) and with different concentrations of TFA (4.35 mM – 43.41 mM) in N<sub>2</sub>-saturated 0.1 M TBAP/MeCN. E<sub>pc</sub><sup>(1)</sup> and E<sub>pc</sub><sup>(2)</sup> indicate the first and second cathodic peak potentials, respectively. Scan rate = 0.1 V/s.



**Fig. 4.** (a) Plot of first reductive peak potentials, E<sub>pc</sub><sup>(1)</sup> at different TFA conc. vs. logarithm of [TFA], 4.35 – 43.41 mM (blue dots). (b) Plot of the logarithm of k<sub>FOWA</sub> obtained from FOWA vs. logarithm of [TFA] within the same concentration range as used in (a).

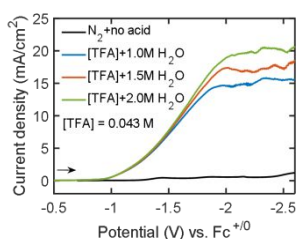
Based on these electrochemical results, we propose a catalytic HER mechanism in which **1**<sup>2+</sup> undergoes two sequential e<sup>–</sup> reduction steps to generate the Ni<sup>0</sup> species **1** (Fig. 5). The protonation (the C step) of **1** can generate **2**, which is tentatively assigned as a (N2S2)Ni<sup>II</sup>-H species. We propose that **2** adopts a square planar geometry where the non-chelating pyridyl group can get protonated or create a hydrogen bond with a TFA molecule, which may explain the greater than 1 order of the reaction in TFA. Furthermore, the protonation of the pyridyl group in the following step could yield complex **3** that can release H<sub>2</sub> and regenerate **1**<sup>2+</sup> upon solvation. Since the pK<sub>a</sub> of TFA is 12.65 in MeCN,<sup>14</sup> while the pK<sub>a</sub> of pyridinium is 12.53 in MeCN,<sup>15</sup> thus it is expected that TFA could protonate one of the pyridyl group in N2S2 even in the presence of a metal ion. Therefore, the pyridyl group of N2S2 could be viewed as mimicking the Cys residue in the Ni-R state of [NiFe]

hydrogenase that can shuttle between a metal-bound state and a protonated state during the HER catalytic cycle.<sup>11</sup>



**Fig. 5.** Proposed catalytic HER cycle (black arrows) for **1**<sup>2+</sup>. The blue arrows include the possible intermediate. HA = TFA.

To evaluate the effect of H<sub>2</sub>O on HER catalysis, we employed a TFA concentration of 0.043 M in MeCN and three different H<sub>2</sub>O concentrations (1.0 M, 1.5 M, and 2.0 M). Linear sweep voltammograms (LSVs) recorded for **1**<sup>2+</sup> under these conditions show plateau currents at potentials lower than -1.75 V, and the shape of the LSVs remained unchanged as more H<sub>2</sub>O was added (Fig. 6).



**Fig. 6.** Linear sweep voltammograms for **1**<sup>2+</sup> recorded in N<sub>2</sub>-saturated 0.1 M TBAP/MeCN in the absence of TFA (blue) and the presence of 0.043 M TFA + different concentration of H<sub>2</sub>O, 1 M (orange), 1.5 M (yellow), and 2.0 M (purple). Scan rate = 0.1 V/s.

FOWA was then carried out at the three different H<sub>2</sub>O concentrations. The average reaction rate constant for the first C step ( $k_{\text{FOWA, avg}}$ ) determined for **1**<sup>2+</sup> is  $1.95 \times 10^5 \text{ s}^{-1}$  (Fig. S18a and Table S2).<sup>12</sup> Notably, these rate constants are independent of the H<sub>2</sub>O concentration (Fig. S18b), and thus the role of H<sub>2</sub>O can be described as mainly impeding the homoconjugation of TFA in MeCN, without interfering with the thermodynamic parameters.<sup>9</sup> Overall, we posit that **3** can produce H<sub>2</sub> mediated by the protonation of the pyridyl group of N2S2, which is less sensitive to how acidic the bulk electrolyte is. Since the FOWA plots deviate from linearity at potentials more negative than -1.6 V, the TOFs determined based on  $k_{\text{FOWA, avg}}$  may significantly overestimate the rate constant at the rate-determining step.<sup>9</sup> <sup>16</sup> Herein, we used Eq. 1,<sup>5b</sup> where  $i_{\text{cat}}$  is the catalytic current density at the plateau current in the presence of 0.043 M of TFA + 2 M H<sub>2</sub>O,  $i_{\text{p}}$  is the peak current density at the Ni<sup>II/I</sup> reduction with no acids, and  $v$  is the scan rate (0.1 V/s), to obtain a catalytic rate constant ( $k_{\text{obs}}$ ) or TOF of  $\sim 1,250 \text{ s}^{-1}$ .

$$k_{\text{obs}} = 1.94 \text{ V}^{-1} \times v \times (i_{\text{cat}}/i_{\text{p}})^2; \quad \text{Eq. 1}$$

The overpotential for the HER process was then calculated using the Appel and Helm method<sup>17</sup> and found to be 730 mV at

$E_{\text{cat}/2}$  for **1**<sup>2+</sup> in the presence of 0.043 M TFA with 1.5 M H<sub>2</sub>O in MeCN. Chronoamperometric experiments carried out for **1**<sup>2+</sup> showed a total charge of 200 mC passed over 15 mins of electrolysis at an applied potential of  $E_{\text{cat}/2}$ , corresponding to  $1.03 \times 10^{-6}$  moles of H<sub>2</sub> (Fig. S13). Bulk electrolysis for **1**<sup>2+</sup> was then performed at  $E_{\text{cat}/2}$  using a carbon cloth electrode and 0.186 mmoles H<sub>2</sub> were detected by GC (Fig. S15), corresponding to a Faradaic efficiency (FE) of 92%. Importantly, complex **1**<sup>2+</sup> was stable during electrolysis, and no color change or formation of precipitate were observed during electrocatalysis, while the CV of the post-electrolysis solution was similar to the CV of **1**<sup>2+</sup> in presence of TFA.

While TFA is a fairly strong acid in MeCN and bare carbon electrodes can perform HER using only TFA at potentials lower than -1 V,<sup>9</sup> the average currents obtained for **1**<sup>2+</sup> during bulk electrolysis were much higher than the background contribution (Fig. S14). The background charge passed during the electrocatalytic HER process in the presence of the bare electrode is about 30% vs. the charge passed in the presence of **1**<sup>2+</sup>, yet the FE of the background HER process is low (< 25%) and does not contribute to more than 10% of the total H<sub>2</sub> produced (Fig. S15). Finally, the HER activity of the rinsed post-electrolysis electrode was identical to that of a clean glassy carbon electrode under the same electrolysis conditions, suggesting that the probed HER process is mainly homogeneous in nature.

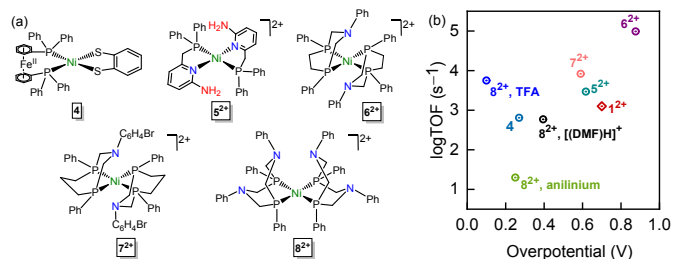
To benchmark the HER activity of **1**<sup>2+</sup>, we selected five efficient Ni<sup>II</sup>-based HER electrocatalysts, **4**,<sup>7</sup> **5**<sup>2+</sup>,<sup>8</sup> **6**<sup>2+</sup>,<sup>5a</sup> **7**<sup>2+</sup>,<sup>5b</sup> and **8**<sup>2+</sup> (Fig. 7a).<sup>6a, 18</sup> We have included the reported TOF values for these electrocatalysts and calculated the overpotentials by correcting the standard thermodynamic potentials ( $E_{\text{HA}}$ ) for H<sup>+</sup>-to-H<sub>2</sub> conversion at the given pK<sub>a</sub> of the acid (HA) used in the corresponding non-aqueous electrolyte (Eq. 2).<sup>9</sup>

$$E_{\text{HA}} = E^0 - (2.303RT/F) \times \text{pK}_a(\text{HA}); \quad \text{Eq. 2}$$

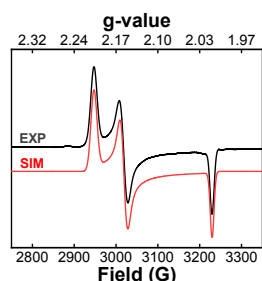
The logTOF values were then plotted vs. the calculated overpotentials ( $E^0 - E_{\text{HA}}$ ) for the Ni complexes mentioned above and **1**<sup>2+</sup> (Fig. 7b). Remarkably, **1**<sup>2+</sup> performs electrocatalytic HER at a higher TOF than those of **4** and **8**<sup>2+</sup>, where **4** used 0.05 M of AcOH in THF<sup>7</sup> and **8**<sup>2+</sup> required  $\leq 0.6$  M of the strong acid anilinium (pK<sub>a</sub> = 10.62 in MeCN)<sup>6a, 9</sup> or 0.25 M of [(DMF)H]<sup>+</sup> in MeCN.<sup>18</sup> While the overpotential for **1**<sup>2+</sup> is higher than those of **4**, **5**<sup>2+</sup>, **7**<sup>2+</sup>, and **8**<sup>2+</sup>, it is lower than that for **6**<sup>2+</sup>, albeit **6**<sup>2+</sup> employs the strong acid [(DMF)H]<sup>+</sup> at concentrations >0.4 M. Overall, the electrochemical HER performance of **1**<sup>2+</sup> is significant, especially since competitive HER kinetics can be achieved at low acid concentration using a weaker acid. The only other Ni HER electrocatalysts containing thiolate and/or pyridine ligands, **4** and **5**<sup>2+</sup>, exhibit TOFs that are comparable to that of **1**<sup>2+</sup>.

We also performed electron paramagnetic resonance (EPR) spectroscopy to detect a Ni<sup>I</sup> species upon reducing **1**<sup>2+</sup> with 1 equiv of CoCp\*<sub>2</sub> (Cp\* = pentamethylcyclopentadienyl). The X-band EPR spectrum in 1:3 MeCN:PrCN (v/v) at 77 K exhibited an EPR signal (Fig. 8) that was simulated using a rhombic g tensor ( $g_x = 2.205$ ,  $g_y = 2.152$ ,  $g_z = 2.012$ ). We attribute this EPR signal to a (N2S2)Ni<sup>I</sup> species such as **1**<sup>+</sup>, suggesting a d<sub>x<sup>2</sup>-y<sup>2</sup></sub> ground state in a square planar geometry, and based also on the comparison with the EPR spectra of other reported Ni<sup>I</sup> complexes,<sup>19</sup> although the formation of a Ni<sup>II</sup> species *in situ* via an oxidative

process cannot be excluded. Intriguingly, the addition of 1 equiv TFA to the *in situ* generated  $1^+$  led to an immediate disappearance of the corresponding EPR signal, further supporting the proposed mechanism in which  $1^{2+}$  can be reduced chemically/electrochemically to generate  $1^+$ , which is reactive toward protons in an organic solvent (Fig. 5).



**Fig. 7.** (a) Selected Ni<sup>II</sup> HER electrocatalysts reported for efficient HER: **4**, **7**, **5**<sup>2+</sup>, **8**, **6**<sup>2+</sup>, **5a**, **7**<sup>2+</sup>, **5b** and **8**<sup>2+</sup>.<sup>6a, 18</sup> (b) Comparison of the logarithm of TOF vs. the calculated overpotential reported for the Ni electrocatalysts shown in (a) and  $1^{2+}$ . The proton sources used are: 0.043 M TFA + 2 M H<sub>2</sub>O in MeCN for  $1^{2+}$ , 0.05 M AcOH in THF for **4**, 0.3 M AcOH in MeCN for **5**<sup>2+</sup>, 0.42 M [(DMF)H]<sup>+</sup> + 1.2 M H<sub>2</sub>O in MeCN for **6**<sup>2+</sup>, 1.26 M [(DMF)H]<sup>+</sup> + 1.09 M H<sub>2</sub>O in MeCN for **7**<sup>2+</sup>. For **8**<sup>2+</sup>, 0.6 M anilinium,<sup>6a</sup> 0.25 M [(DMF)H]<sup>+</sup>, or 1.8 M TFA in MeCN<sup>18</sup>.



**Fig. 8.** Experimental (black) and simulated (red) EPR spectra for  $1^{2+}$  after treating it with 1 equiv. of CoCp<sub>2</sub>\* in 1:3 MeCN:PrCN glass at 77 K. The following g values were used for the simulation:  $g_x = 2.205$ ,  $g_y = 2.152$ ,  $g_z = 2.012$ .

In summary, we have synthesized and characterized a bioinspired complex [(N2S2)Ni(MeCN)<sub>2</sub>]<sup>2+</sup>,  $1^{2+}$ , that is an efficient HER electrocatalyst. This complex catalytically reduces protons to H<sub>2</sub> at low acid concentration. Given that most of the reported Ni-based molecular HER electrocatalysts perform HER using stronger acids than TFA, and often at high acid concentration,<sup>5-6</sup> the performance of  $1^{2+}$  is remarkable as it achieves a high TOF for the HER. In addition, we highlight the role of the pendant pyridyl group of the N2S2 ligand in leading to elevated HER kinetics, which we consider resembles the proton-relay role of the Cys residue in [NiFe] hydrogenases that can also shuttle between a metal-bound and a protonated state. Although  $1^{2+}$  catalyzes the HER process at a high overpotential, 0.7 V, the proposed HER mechanism should inspire the development of improved bioinspired HER electrocatalysts that operate under benign reaction conditions.

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## Author Contributions

# These authors contributed equally.

## Conflicts of interest

There are no conflicts to declare.

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## COMMUNICATION