Nickel Pyridinethiolate Complexes as Catalysts for the Light-Driven Production of Hydrogen from Aqueous Solutions in Noble-Metal-Free Systems

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ABSTRACT: A series of mononuclear nickel(II) thiolate complexes (Et₄N)Ni(X-pyS)₃ (Et₄N = tetraethyalammonium; X = 5-H (1a), 5-Cl (1b), 5-CF₃ (1c), 6-CH₃ (1d); pyS = pyridine-2-thiolate), Ni(pySH)₄(NO₃)₂ (2), (Et₄N)Ni(4,6-Y₂-pymS)₃ (Y = H (3a), CH₃ (3b); pymS = pyrimidine-2-thiolate), and Ni(4,4′-Z-2,2′-bpy)(pyS)₂ (Z = H (4a), CH₃ (4b), OCH₃ (4c); bpy = bipyridine) have been synthesized in high yield and characterized. X-ray diffraction studies show that 2 is square planar, while the other complexes possess tris-chelated distorted-octahedral geometries. All of the complexes are active catalysts for both the photocatalytic and electrocatalytic production of hydrogen in 1/1 EtOH/H₂O. When coupled with fluorescein (Fl) as the photosensitizer (PS) and triethylamine (TEA) as the sacrificial electron donor, these complexes exhibit activity for light-driven hydrogen generation that correlates with ligand electron donor ability. Complex 4c achieves over 7300 turnovers of H₂ in 30 h, which is among the highest reported for a molecular noble-metal-free system. The initial photochemical step is reductive quenching of Fl* by TEA because of the latter’s greater concentration. When system concentrations are modified so that oxidative quenching of Fl* by catalyst becomes more dominant, system durability increases, with a system lifetime of over 60 h. System variations and cyclic voltammetry experiments are consistent with a CECE mechanism that is common to electrocatalytic and photocatalytic hydrogen production. This mechanism involves initial protonation of the catalyst followed by reduction and then additional protonation and reduction steps to give a key Ni−H*/N−H* intermediate that forms the H−H bond in the turnover-limiting step of the catalytic cycle. A key to the activity of these catalysts is the reversible dechelation and protonation of the pyridine N atoms, which enable an internal heterocoupling of a metal hydride and an N-bound proton to produce H₂.

INTRODUCTION

The splitting of water into its constituent elements to produce H₂ as a clean, non-carbon-containing fuel and O₂ as the oxidation product represents a promising way to store and convert solar energy in chemical bonds.1−3 In such an artificial photosynthetic (AP) scheme, the reductive side of water splitting is the light-driven generation of hydrogen from aqueous protons. A major challenge is finding noble-metal-free catalysts and combining them with highly absorbing photosensitizers (PS) into a robust system for efficient proton reduction into H₂.4−5 In schemes for the proton reduction half-reaction, electrons are provided chemically by a sacrificial reductant in a manner that allows the steps leading to hydrogen generation to be delineated and studied in detail. The sacrificial electron donor in the homogeneous system thus replaces the oxidative side of a complete AP scheme, enabling simpler optimization of proton reduction.

Great progress has been achieved over the last 5 years in the design, synthesis, and study of new catalysts for photochemically driven proton reduction.6−11 For example, cobaloxime catalysts when coupled with a variety of PS have been found to generate hydrogen using visible light.12−18 However, these systems are relatively short-lived (<6 h) and may exhibit low catalytic turnover numbers (TON) (<400 without extra ligand). For the cobaloxime-containing systems, these problems arise from conversion of the catalyst to an inactive form, possibly by ligand decomposition or hydrogenation,18 and from ligand exchange reactions that occur when the Co ion traverses oxidation states in which the ligands are labile.19 Nickel(II) bis(diphosphine) complexes, which were originally found to be effective electrocatalysts for proton reduction by DuBois and co-workers,20−22 are also durable catalysts for photocatalytic hydrogen generation, although they exhibit relatively low turnover frequencies (TOF) (<20 h⁻¹).23 A nickel 2-mercaptopthenol complex was found by Rong and co-workers to be an active catalyst with a quantum efficiency as high as 12.3% at 460 nm (based on one photon per H₂ molecule).24 However, the TON of this catalyst is lower than 100. In more recent work from our laboratories, systems containing cobalt...
bis(dithiolene) complexes as catalysts exhibit up to 9000 TON and a TOF of 3400 h⁻¹.²⁵,²⁶ A TON of 4400 was found recently using a pentadentate polypyridine cobalt catalyst in aqueous media.²⁷ Another cobalt pentapyridine electrocatalyst from Long and Chang²⁸ was found to generate hydrogen photochemically at neutral pH in water with a TON of ~100.²⁹ Many other homogeneous systems use a photosensitizer containing a rare platinum-group element, but still most activity is lost within 10 h of irradiation.⁶

In another recent study, we reported a robust noble-metal-free system using a nickel pyridinethiolate catalyst (1a; Figure 1) with a fluorescein (Fl) photosensitizer, and this system achieved over 5000 TON when coupled with triethylamine (TEA) as the sacrificial electron donor.³⁰ This catalyst has a bioinspired aspect, because the nickel ion has mixed N/S ligation as found in the nickel–iron hydrogenases.³¹–³³ Chen and co-workers later found that binuclear nickel 2-mercaptobenzimidazole and 2-mercaptobenzothioazole complexes gave TON values of 320 when using Fl as photosensitizer.³⁴ In this paper, we report a series of nine related nickel thiolate complexes and study their activities for both photocatalytic and electrocatalytic proton reduction. The photochemical pathway for hydrogen generation has been found to proceed by initial reductive quenching of the excited photosensitizer (PS⁎). The relative activities of the catalysts, their electrochemical behaviors, and NMR spectroscopic results give insight into the mechanisms of the catalytic processes. Overall, these studies are significant because they show mechanistic detail and trends that will guide continued photocatalyst and electrocatalyst innovations for solar energy utilization.

Results

Synthesis and NMR and Electronic Absorption Spectra of the Nickel Thiolate Complexes. Complexes 1b–d, 2, and 3a,b were synthesized by adding 3–4 equiv of the corresponding thiol to the nickel precursor (Ni(NO₃)₂ or (Et₄N)₂[NiCl₄]) under N₂.³⁵ For complexes 4a–c, formation of the complex was achieved by slow addition of the corresponding 2,2'-bipy derivative, followed by 2 equiv of the ligand as its thiol (pySH) to give air-stable complexes with crystallized yields of 49–93%. The ¹H NMR spectra of paramagnetic complexes 1, 3, and 4 show broad proton resonances ranging from δ ~11 to 140 ppm, while complex 2 exhibits sharp, well-defined peaks in the aromatic region (consistent with diamagnetism (see Figures S1–S10, Supporting Information). On the other hand, the magnetic moment for complex 3b (as determined by the Evans method³⁶) is 3.0 ± 0.2 μB, which is consistent with octahedral Ni(II) (S = 1). The UV–vis absorption spectra of the green complexes 1a–d, 2, and 3a,b and the brown-orange complexes 4a–c were measured at room temperature in MeCN (see Table 1 for data

![Figure 1. Nickel thiolate complexes. In anionic complexes, the counterion is Et₄N⁺; in cationic complexes, the counterion is NO₃⁻.](image)

Table 1. Electronic Absorptions for Complexes 1a–d, 2, 3a,b, and 4a–c in Acetonitrile

<table>
<thead>
<tr>
<th>complex</th>
<th>λ&lt;i&gt;max&lt;/i&gt; nm (ε, M⁻¹ cm⁻¹)</th>
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<tbody>
<tr>
<td>1a</td>
<td>623 (36), 287 (37900)</td>
</tr>
<tr>
<td>1b</td>
<td>625 (34), 293 (39600)</td>
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<tr>
<td>1c</td>
<td>623 (40), 298 (43500)</td>
</tr>
<tr>
<td>1d</td>
<td>689 (22), 237 (21300)</td>
</tr>
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<td>2</td>
<td>634 (28), 371 (32700), 291 (82500)</td>
</tr>
<tr>
<td>3a</td>
<td>611 (47), 285 (36800)</td>
</tr>
<tr>
<td>3b</td>
<td>665 (33), 269 (38800)</td>
</tr>
<tr>
<td>4a</td>
<td>283 (29200)</td>
</tr>
<tr>
<td>4b</td>
<td>284 (32600)</td>
</tr>
<tr>
<td>4c</td>
<td>282 (32900)</td>
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</table>

*From ref 35.*

and Figures S11–S14 (Supporting Information) for spectra). Complexes 1a–d, 2, and 3a,b all exhibit a broad low-energy band with a maximum between 610 and 690 nm having a molar absorption coefficient ε under 50 L mol⁻¹ cm⁻¹, which corresponds to a spin-allowed d–d transition of pseudooctahedral Ni(II).³⁵,³⁶ Complexes 1a–c have this band at ~623 nm, while the band shifts to 689 nm for complex 1d. A similar shift from 611 to 665 nm is also observed for complexes 3a,b. Complexes 1a–d, 2, 3a,b, and 4a–c all exhibit high-energy bands in the UV region with ε values on the order of 10⁴ L mol⁻¹ cm⁻¹, corresponding to spin-allowed intraligand (π–π⁎) transitions.³⁵

Structural Studies. The solid-state molecular structures of 1b–d, 2, 3a,b, and 4a–c were determined by single-crystal X-ray crystallography (see Figure 2 and the Supporting Information), and selected bond lengths and angles are given in Tables 2–9, respectively. Complex 2 possesses a square-planar geometry, as expected from the diamagnetism. In the structure, the four pySH ligands coordinate to Ni through the thiolate donors, and the pyridine nitrogen atoms of each ligand are protonated and uncoordinated. NH···O hydrogen bonding between the pySH ligand and NO₃⁻ counteranion is also observed (see the Supporting Information), but no NH···S hydrogen bonding. All of the other complexes have pseudo-octahedral geometries that are distorted as a consequence of four-membered χ²N,S-chelate rings. In the solid-state structures, complexes 1a,b and 3a are found as the mer isomers, whereas complexes 1d and 3b (which have methyl groups next to the coordinated pyridyl nitrogen atoms) have a fac arrangement of the donor N and S atoms. The bond angles in all of these complexes are essentially the same for different pyridinethiolate and pyrimidinethiolate ligands. The four-membered N,S-chelate rings have a N–Ni–S bond angle of ~68°, while for the five-membered N,N-chelate ring involving bipyridyl ligands the bite angle is ~78°. For complex 1d relative to 1a, the Ni–S bond distance is shortened by ~0.04 Å and the corresponding Ni–N bond distance is lengthened by ~0.05 Å as a consequence of the pyS ligand having a methyl...
group at the 6-position of the py ring. A similar trend is observed for complexes 3a,b. Each of these structural differences is attributed to the steric hindrance of the methyl group cis to the N donor. The square-planar complex 2 has significantly shorter (by 0.25 Å) Ni–S bond lengths relative to the distorted-octahedral complexes. For complexes 4a–c, the Ni–N and Ni–S (N and S both on pyS ligand) distances are indistinguishable across the series, whereas the Ni–N bpy distances become shorter by ~0.03 Å in going from 4a to 4c.

Photocatalytic Hydrogen Production. A series of photocatalytic experiments using complexes 1a–d, 2, 3a,b, and 4a–c for hydrogen production were performed using a solution of TEA (0.36 M) as the sacrificial donor, Fl (2.0 mM) as the photosensitizer, and the nickel complex (4.0 μM) as the H2-generating catalyst in EtOH/H2O (1/1) with a green-light-emitting diode (LED; λ 520 nm, 13 mW/cm²) at 15 °C. The amount of H2 produced was monitored in real time by the pressure change in the reaction vessel and quantified at the end.
of the photolysis by GC analysis of the headspace gases. The TON and TOF values for hydrogen production for the different complexes are given in Table 10. Omission of any of the three components leads to no significant H₂ production.

### Table 2. Key Distances and Angles in 1b

<table>
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<th>Bond Distances (Å)</th>
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<td>Ni(1)−S(1) 2.4983(15) Ni(1)−N(1) 2.059(4)</td>
<td>S(1)−Ni(1)−N(1) 68.02(12) S(3)−Ni(1)−N(3) 68.43(13)</td>
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<td>Ni(1)−S(2) 2.4909(16) Ni(1)−N(2) 2.040(4)</td>
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<td>Ni(1)−S(3) 2.5019(15) Ni(1)−N(3) 2.038(4)</td>
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### Table 3. Key Distances and Angles in 1d

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<td>Ni(1)−S(1) 2.4545(6) Ni(1)−N(1) 2.1069(17)</td>
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<td>Ni(1)−S(2) 2.4698(6) Ni(1)−N(2) 2.1088(17)</td>
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<td>Ni(1)−S(3) 2.4718(6) Ni(1)−N(3) 2.1145(17)</td>
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<td>Ni(1)−S(1) 2.2134(8) Ni(1)−S(3) 2.2142(8)</td>
<td>S(1)−Ni(1)−S(2) 94.15(3) S(3)−Ni(1)−S(4) 97.82(3)</td>
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<td>Ni(1)−S(2) 2.2154(8) Ni(1)−S(4) 2.2036(8)</td>
<td>S(2)−Ni(1)−S(3) 84.45(3) S(4)−Ni(1)−S(1) 83.67(3)</td>
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### Table 5. Key Distances and Angles in 3a

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<td>Ni(1)−S(2) 2.4146(3) Ni(1)−N(2) 2.0755(12)</td>
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### Table 6. Key Distances and Angles in 3b

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<td>Ni(1)−S(2) 2.4535(5) Ni(1)−N(2) 2.1142(14)</td>
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<td>Ni(1)−S(3) 2.4368(6) Ni(1)−N(3) 2.1020(16)</td>
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### Table 7. Key Distances and Angles in 4a

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<td>Ni(1)−S(1) 2.5516(7) Ni(1)−N(2) 2.0594(15)</td>
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<td>Ni(1)−N(1) 2.0418(15) Ni(1)−N(4) 2.0693(15)</td>
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### Table 8. Key Distances and Angles in 4b

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<td>Ni(1)−S(1) 2.4801(5) Ni(1)−N(2) 2.0457(13)</td>
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<td>Ni(1)−S(2) 2.5300(5) Ni(1)−N(3) 2.0653(13)</td>
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<td>Ni(1)−N(1) 2.0553(13) Ni(1)−N(4) 2.0699(13)</td>
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### Table 9. Key Distances and Angles in 4c

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<td>Ni(1)−S(1) 2.4814(9) Ni(1)−N(2) 2.052(3)</td>
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<td>Ni(1)−S(2) 2.5400(9) Ni(1)−N(3) 2.050(3)</td>
<td>S(2)−Ni(1)−N(2) 67.66(8)</td>
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<td>Ni(1)−N(1) 2.058(3) Ni(1)−N(4) 2.064(3)</td>
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### Table 10. Photocatalytic and Electrocatalytic Hydrogen Production and ¹H² Quenching Data for Complexes 1a−d, 2, 3a,b, and 4a−c

<table>
<thead>
<tr>
<th>complex</th>
<th>TON(30 h)</th>
<th>initial TOF, h⁻¹</th>
<th>E(ν, Å)</th>
<th>E(ν, Å)</th>
<th>kν M⁻¹ s⁻¹</th>
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<tbody>
<tr>
<td>1a</td>
<td>3750 ± 300</td>
<td>258 ± 21</td>
<td>−1.18</td>
<td>−1.61</td>
<td>5.85 × 10⁷</td>
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<tr>
<td>1b</td>
<td>3420 ± 274</td>
<td>220 ± 18</td>
<td>−1.32</td>
<td>−1.70</td>
<td>9.36 × 10⁷</td>
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<tr>
<td>1c</td>
<td>2282 ± 160</td>
<td>160 ± 11</td>
<td>−1.32</td>
<td>−1.71</td>
<td>9.38 × 10⁷</td>
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<tr>
<td>1d</td>
<td>5020 ± 450</td>
<td>371 ± 33</td>
<td>−1.26</td>
<td>−1.61</td>
<td>1.26 × 10⁸</td>
</tr>
<tr>
<td>2</td>
<td>3520 ± 281</td>
<td>191 ± 15</td>
<td>−1.33</td>
<td>−1.56</td>
<td>1.32 × 10⁸</td>
</tr>
<tr>
<td>3a</td>
<td>1660 ± 158</td>
<td>103 ± 11</td>
<td>−1.00</td>
<td>−1.64</td>
<td>1.21 × 10⁹</td>
</tr>
<tr>
<td>3b</td>
<td>3730 ± 317</td>
<td>254 ± 21</td>
<td>−1.26</td>
<td>−1.67</td>
<td>5.16 × 10⁹</td>
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<tr>
<td>3c</td>
<td>3095 ± 250</td>
<td>168 ± 14</td>
<td>−1.36</td>
<td>−1.58</td>
<td>3.87 × 10⁹</td>
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<tr>
<td>3d</td>
<td>4297 ± 322</td>
<td>265 ± 20</td>
<td>−1.44</td>
<td>−1.69</td>
<td>2.50 × 10⁹</td>
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<tr>
<td>3e</td>
<td>7335 ± 645</td>
<td>312 ± 35</td>
<td>−1.46</td>
<td>−1.70</td>
<td>1.72 × 10⁹</td>
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</table>

In 1/1 EtOH/H₂O (vs SCE). In 8/1/1 DMF/ EtOH/H₂O (vs SCE). In 1/1 MeOH/H₂O (vs SCE).
second reducing electron so that each TEA yields two electrons for the H₂ produced.

The two pyrimidinethiolate nickel complexes 3a−b also exhibit good activity for H₂ generation (see Table 10 and Figure S16 (Supporting Information)), with the methylated derivative being substantially more active. A similar trend is also observed with the mixed ligand nickel complexes 4a−c with activity increasing in the order 4a < 4b < 4c (see Table 10 and Figure S17 (Supporting Information)). The substituents on the bipyridine ligands give evidence of electronic effects on reactivity. For example, complex 4c with the most electron donating substituents (R = OMe) exhibits the highest catalytic activity, achieving 7335 TONs of hydrogen/mol of catalyst after 30 h of irradiation. For comparison, the tris(bipyridyl) nickel complex [Ni(bpy)₃](PF₆)₂ exhibits no H₂ production activity under the same conditions (see the Supporting Information), underscoring the importance of the pyridine-thiolate ligand.

The ratio of Ni to pyS ligand was also examined in the course of the photochemical studies, as shown in Figure 4. In the absence of pyridinethiolate ligand, Ni(NO₃)₂ was inactive for the generation of hydrogen. Addition of pySH to the system led to increasing activity up to a maximum of 3 equiv of pyS per Ni(II) ion. Further addition of pySH (giving a ratio of 5/1 ligand/Ni(II)) yielded no greater activity. The addition of pyridine rather than pyridinethiolate led to some activity for H₂ formation, but the turnover number, 420 TON in 16 h, was substantially lower than the activity exhibited by the Ni/pyS system, as shown in Figure 4.

**Electrocatalytic Studies of the Nickel Catalysts.** Cyclic voltammetric experiments were conducted in both aqueous and organic solvent media for complexes 1a−d, 2, 3a,b, and 4a−c. In dry DMF, no reduction peaks for complexes 1a−c and 3a,b were seen at potentials less negative than −2 V (vs SCE), whereas for complexes 1d, 2, and 4a−c, irreversible reduction peaks are seen at −1.27, −1.33, −1.48, −1.57, and −1.61 V, respectively. However, reduction peaks for all of the complexes are observable when the complex is dissolved in a 1/1 alcohol/H₂O mixture (Figure 5 for 1a−d, 2, and 3a,b in 1/1 EtOH/H₂O and Figure 6 for complexes 4a−c in 1/1 MeOH/H₂O).

To examine these complexes as potential electrocatalysts for H₂ production, 8 equiv of acetic acid was added to each complex solution and the system was examined by cyclic voltammetry. Significant current enhancement is observed near the onset of the original complex reduction peak for all of the complexes (Figures 5 and 6). A control experiment without the

![Figure 3](image1.png)  
**Figure 3.** Hydrogen production from systems containing nickel complexes 1a−d (4.0 μM), Fl (2.0 mM), and TEA (0.36 M) in EtOH/H₂O (1/1) at pH 11.6 upon irradiation with a λ 520 nm LED (13 mW/cm²) at 15 °C.

![Figure 4](image2.png)  
**Figure 4.** Hydrogen production from systems containing Ni(NO₃)₂ (4.0 μM), Fl (2.0 mM), and TEA (0.36 M) in EtOH/H₂O (1/1) at pH 11.6 upon irradiation with a λ 520 nm LED (13 mW/cm²) at 15 °C with no added ligand (black), [py] = 20 μM (dark green), [pyS] = 4.0 μM (blue), [pyS] = 12 μM (green), and [pyS] = 20 μM (red).

![Figure 5](image3.png)  
**Figure 5.** Cyclic voltammograms of 0.1 mM of catalysts 1a (a), 1b (c), 1c (d), 1d (e), 2 (f), 3a (g), and 3b (h) in 1/1 EtOH/H₂O without acid (black) and in the presence of 0.8 mM acetic acid (red) and a control with 0.8 mM acetic acid in the absence of catalyst (b). Conditions: 0.1 M KNO₃, glassy carbon as both working and counter electrodes, scan rate 100 mV/s.
nickel complex but with the same amount of added acetic acid in the same solvent mixture shows a much lower current enhancement (Figures S5b and 6b). For complexes 4a c, which have better solubility and stability in MeOH/H2O mixtures, a typical series of voltammograms were obtained with increasing amounts of acetic acid added (Figure 6).

Cyclic voltammetric studies were also carried out on complexes 1a d, 2, 3a b, and 4a c in an 8:1:1 DMF/ EtOH/H2O mixture as a function of acid concentration with sequential additions of acetic acid (Figure 7 for 1d and Figures S18 S26 (Supporting Information) for other complexes). For all of these complexes, a new reduction wave is observed upon addition of 1 equiv of acid between 1.0 and 1.2 V (vs SCE), which is more positive (less cathodic) than the catalytic wave. However, this wave does not show any catalytic feature upon further addition of acid and disappears after neutralization with TEA (Figures S27 and 28 (Supporting Information)). The observed catalytic current (i ) has a linear correlation with respect to added acetic acid concentration at a scan rate of 0.1 V/s. The observed i feature in the 8:1:1 DMF/EtOH/H2O mixed solvent is 400 mV more negative than the corresponding i value found in systems having the 1/1 alcohol/H2O mixed solvent (Table 10).

Fluorescence Quenching of Fl by Nickel Catalysts. The photochemically driven electron-transfer steps were studied through Fl quenching by complexes 1a d, 2, 3a b, and 4a c in 1/1/8 EtOH/H2O/DMF solvent mixtures at pH 11.6 (DMF used for higher solubility of the nickel complexes; the quenching rate constant was found to be independent of the ratio of the solvent components30). The fluorescence of Fl (excited at 460 nm) is quenched by all of the nickel complexes following linear Stern Volmer behavior with near-diffusion-controlled rates on the order of 1010 M s1 (Table 10 for quenching rates and Figures S29 S37 (Supporting Information) for the linear plots).

1H NMR Studies on Catalyst Protonation. To study the protonation of the nickel complexes, 1H NMR spectra were recorded in d6-DMSO with the addition of acid. The paramagnetically shifted spectra of 1d show that the four proton peaks of the complex shift significantly upon addition of 1 equiv of trifluoroacetic acid (Figure S38 (Supporting Information)) and that the change is reversible. The addition of TEA as a base leads to complete recovery of the initial resonances. The protonation/deprotonation also correlates with the observed color change from green to orange and back to green. A similar result for complex 1a was also observed (Figure S39 (Supporting Information)).

### DISCUSSION

**Initial Photochemical Steps.** In an earlier report of the complex (NEt4)[Ni(pyS)3] (1) as the catalyst for H2 generation in a system containing Fl as the photosensitizer and TEA as the sacrificial electron donor, mechanistic proposals were presented regarding the initial photochemical steps and subsequent electron and proton transfers leading to H2 formation.30 The present discussion expands on that analysis to include the additional mechanistic data described here.

With regard to the initial photochemical step, electron transfer quenching of Fl by either TEA (reductive quenching to form Fl+ + TEA) or Ni catalyst (presumably oxidative quenching to form Fl+ + Ni catalyst) is possible, but the relative concentrations of sacrificial donor and Ni catalyst determine the primary photochemical path followed upon irradiation. The rate constant for the reductive quenching by TEA has been reported previously by us to be 5.5 × 107 M s1.30 For all of the Ni complexes reported here (1a d, 2, 3a b, and 4a c), the Fl quenching rate constants (kq) were determined from linear fits of the Stern Volmer equation (Table 10). These quenching rate constants are near the diffusion-controlled limit and range from 5.8 × 109 to 3.9 × 1010 M s1. However, even though the quenching rate constants by the Ni catalysts are 2 3 orders of magnitude greater than the reductive quenching rate constant by TEA, the primary electron-transfer quenching path from the Fl excited state is via reaction with TEA, since the electron donor’s concentration (0.36 M) is 104 times greater than that of the Ni catalyst (4 × 106 M) employed in the system.

The subsequent electron transfer from Fl to the catalyst was also critical for the effectiveness and durability of the system. The prior report of the Fl/1a/TEA system found that if the catalyst was not present for reduction by Fl, the dye decomposed rapidly (within 20 30 min).30 With catalyst

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**Figure 6.** Cyclic voltammograms of 0.5 mM of catalysts 4a (a), 4b (c), and 4c (d) in 1/1 MeOH/H2O without acid (black) and with [acetic acid] = 1.0 mM (dark green), 2.0 mM (brown), 3.0 mM (blue), 4.0 mM (green), and 5.0 mM (red) and a control with 5.0 mM of acetic acid in the absence of catalyst (b). Conditions: 0.1 M KNO3, glassy carbon as both working and counter electrodes, scan rate 100 mV/s.

**Figure 7.** Cyclic voltammograms of 1.0 mM of catalyst 1d in 8/1/1 DMF/EtOH/H2O without the presence of acid (black) and in the presence of acetic acid with increasing concentration (other colors). Inset: plot of i taken from the peak plateau versus [acetic acid]. Conditions: 0.1 M TBA PF6 glassy carbon as both working and counter electrodes, scan rate 100 mV/s.

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present, the major F1 absorption lasted for many hours, consistent with rapid electron transfer from PS− relative to PS−

decomposition.

The reductive quenching pathway involving PS* and the
electron donor, and the subsequent electron transfer from PS−
to the catalyst, have been described in other reported three-
component homogeneous photocatalytic systems for H2

generation.6 In those systems, the organic PS was either
Eosin Y or chalcogen-substituted rhodamine dyes1,6,30 with a
long-lived 3ππ* excited state, and the catalyst was a cobaloxime
derivative. In those systems, the dye bleached within minutes
under irradiation in the presence of the sacrificial donor without
any catalyst present. However, addition of catalyst greatly
prolonged the durability of the PS by allowing electron transfer
from PS− to the catalyst and subsequent proton reduction to H2.

To examine this analysis further in the present system, the
TEA concentration was reduced to 7.0 mM to slow the
reductive quenching rate and determine the potential viability
of an oxidative quenching path. Catalyst 4a, which has the
highest quenching rate constant, was used in this experiment at
0.05 mM concentration. In this case, the oxidative quenching
rate is calculated from kq (quencher) to be ~5 times faster than
the reductive quenching rate. After depletion of TEA for H2

generation, the system was regenerated by adding more TEA, with
the system lasting over 60 h (Figure S40 (Supporting
Information)). A control experiment using 0.36 M instead of
7.0 mM [TEA] lasted only 15 h.

The result supports the hypothesis that a more stable organic
dye containing system for H2 could be obtained if either (1) the
photochemical step of PS* involved electron transfer to the
catalyst rather than reduction of PS* by the electron donor or
(2) the reduced dye PS− was stable to decomposition. It is also
notable that in the present system the quenching of the dye
occurred from its 1ππ* excited state rather than from the
corresponding 3ππ* state, indicating that bimolecular quenching
can compete with radiative and nonradiative decay for
certain dyes. The exploration of new systems containing
organic PS* that can transfer electrons directly to the catalyst
(before reduction by the sacrificial donor) thus seems compelling.

Mechanism of Catalysis in Proton Reduction. We have
previously proposed a mechanism for proton reduction by the
nickel complex in which protonation of the pyS ligand
generates the active catalyst, which is subsequently reduced
from formally Ni(II) to Ni(I). However, the later steps in
the mechanism were less clear. Here, the additional electrochemical
studies and substrate effects point toward a CECE
mechanism for proton reduction and H2 formation.

For the nickel complexes 1a−c and 3a in 8/1/1 DMF/
EtOH/H2O, the CV shows no reduction peak at potentials less
negative than ~2.0 V (vs SCE), indicating that the complexes
cannot accept an electron from 1Fl* in this solvent mixture.
However, upon addition of acetic acid to the nickel complexes
1a−c and 3a, two reduction peaks are observed in the
voltammogram (Supporting Information). There is no catalytic
wave observed for the peak at the more positive potential. We
tentatively assign this peak to a “Ni(II)−H+/Ni(I)−H” couple
formed in situ through protonation of the original complexes.
Despite the use of the “Ni(II)−H+/Ni(I)−H” designation for
this couple, the site of protonation is not specified at this point
but is discussed further below.

Even though complexes 1d, 3b, and 4a−c show an
irreversible reduction wave before addition of acid, a new
wave at slightly more positive potential is observed upon
addition of 1 equiv of acid (Supporting Information). This
wave is at a potential similar to the proposed “Ni(II)−H+/Ni(I)−H” couple of complexes 1a−c and 3a. For the
protonated complex 2, an irreversible reduction wave is seen
in the absence of acid and remains essentially unchanged upon
the addition of acid (a slight shift to more a positive potential
may be due to a change of pH).

For all of the complexes the catalytic wave appears more
negative of the first reduction wave. This observation is
consistent with the need for protonation of the catalysts (except
for 2, which is already protonated) for reduction to occur
followed by an additional protonation and reduction for
hydrogen production.

To examine this hypothesis further in more aqueous media,
CVs were recorded in a 1/1 alcohol/H2O mixture at 0.1 mM
catalyst concentration (Figures 5 and 6). In each case, an
irreversible reduction peak was observed in the absence of acid.
A catalytic wave grew in for each of the complexes upon
addition of 8 equiv of acetic acid, indicating that they are active
proton reduction catalysts in this solvent. The color change
from green (in DMF) to orange (in 1/1 alcohol/H2O) for
complexes 1a−d and 3a,b is associated with their initial
protonation of the complexes, as indicated in step 1 of Scheme
1. This protonation step was supported further by 1H NMR

spectroscopy of complexes 1a,d (Figure 7 and Supporting
Information). Addition of 1 equiv of trifluoroacetic acid to each
complex gave rise to new paramagnetically shifted resonances,
while addition of TEA as a base returned each sample back to
its original spectrum. Thus, the protonation of these complexes
is reversible.

The site of protonation suggested in Scheme 1 on nickel
complexes 1a−d, 3a,b, and 4a as the pyridyl N with ligand
dehalation is a matter of conjecture. Although isolation of the
orange protonated species indicated above was not successful,
the structure of 2 obtained with 4 equiv of protonated pyS
ligand clearly shows that the dehalation of each ligand was
associated with the protonation of each pyridyl N. As noted
above, complex 2 has photocatalytic activity for hydrogen
production identical with that of 1a (Supporting Information),
which suggests similar intermediates are formed during catalysis
starting from both complexes. Importantly, we found that
complex 2 can be converted into 1a by addition of NaOH as base in MeOH. This process was observed by 1H NMR spectroscopy, and only 1a as the product was observed (see the Supporting Information). In the structure of 2, the four pyridyl rings are bent toward the nickel center and the distances between the proton (on the pyridine N atom) and the Ni(II) ion range from 2.86 to 3.08 Å, which is slightly shorter than the 3.32 Å reported for the Fe(II) ion range from 2.86 to 3.08 Å, which is slightly shorter than the

between the proton (on the pyridine N atom) and the Ni(II) ion range from 2.86 to 3.08 Å, which is slightly shorter than the 3.32 Å reported for the Fe(II)−H−N distance in an [Fe−Fe] hydrogenase mimic.38 Thus, it is proposed that the site of initial protonation in these complexes is the pyridyl N with dechelation and that proton transfer from this ligand is important for H2 generation.

We have noted that, with further addition of acetic acid, a catalytic wave is seen at a more negative potential than the “Ni(II)−H+/Ni(I)−H−” couple. This observation is consistent with the proposed mechanism involving further reduction of the initial “Ni(I)−H” intermediate for hydrogen production. The catalytic peak current follows a linear correlation with respect to [acetic acid] for all these complexes (Figure 7 and Supporting Information), indicating the reaction rate has a second-order dependence on [H+].39 This implies that the second protonation step occurs at or before the turnover-limiting step (Scheme 1, step 3). The second reduction, at which the catalytic current is seen, leads to formation of a proposed Ni hydride intermediate. In the photochemical reaction, the electron for this reduction is supplied by a second Fl− or by the decomposition of TEA.

Structural support for the proposed hydride intermediate in Scheme 1 and the role of pyridinethiolate as a proton shuttle comes from work by Morris and co-workers, who described an Ir(pyS) complex that undergoes heterolytic splitting of dihydrogen to form a metal hydride and protonated pyS.40 In the case of the IrH(pySH) complex heterolytic activation of H2 is preferred, whereas in the case of the Ni(pyS) complexes, H2 evolution is preferred, probably from differences in the M−H bond energies (BDE(Ir−H) > (BDE(Ni−H))).

The coordination modes of the pyS ligand on Ni seen in the structures of the tris(pyridinethiolate) Ni complexes and the square-planar complex 2 are consistent with computational studies of ligand protonation and dechelation.41 Dechelation to generate a pendent nitrogen base for proton acceptance and delivery to the metal center are similar to those proposed for proton reduction/hydrogen oxidation in [Fe−Fe] hydrogenases,32,42−44 [Fe−Fe] hydrogenase mimics,38 and some nickel bis(diphosphine) catalysts.

The CECE mechanism that is proposed in Scheme 1 for the Ni pyridinethiolate complexes during hydrogen production differs slightly from the ECEC mechanism proposed by Helm and co-workers45 for Ni bis(diphosphine) complexes, in which the diphosphine has a single pendant amine. The difference in the initial step during catalysis for these two classes of catalysts could be due to the different charges on the complexes. The Ni pyridinethiolate complexes have an overall 1− or 0 charge and thus favor an initial protonation step, while the Ni bis(diphosphine) complexes have an overall 2+ charge and favor reduction first. There is also a difference in turnover-limiting steps: Helm and co-workers found that the turnover-limiting step is the first protonation of the Ni(I) species.45 The different mechanism from the reported complexes here could be due to the high-spin electronic configuration, which gives more labile ligands and rapid dechelation of the four-membered Ni(pyS) ring, speeding the initial protonation.

In view of the difference in the pH of the photochemical and electrochemical experiments, there may be different degrees of catalyst protonation prior to each reduction step. However, insight into protonation prior to the initial reduction step was obtained by monitoring the UV−vis spectra of complex 1a in going from pH 11.5 to pH 5.2. Isosbestic points were observed over this range (Figure S42 (Supporting Information)), indicating that over this range only two species are present: the unprotonated complex and the singly protonated complex with one unchelated ligand. Therefore, the simplest interpretation is that the initial CE steps at the catalyst for photochemical and electrochemical H2 formation are the same. However, further study is needed to determine if differences exist in the rest of the catalytic cycle.

Ligand Dependence of Catalytic Activity. The present study also shows the dependence of catalytic activity as a function of ligand electronic factors in light-driven H2 production. In this study, Ni tris(pyridinethiolate) (1a−d), tris(pyrimidinethiolate) (3a,b), and bipyridine bis(pyridinethiolate) (4a−c) complexes and tetrakis(pyridinethiolate) complex 2 were examined as catalysts for the photo- and electrochemically driven generation of H2. For these catalysts under identical photolysis conditions, both the catalystTON and initial TOF correlate with ligand electron-donating ability. For example, the TON and TOF for 1c, 3a, and 4a, which have electron-withdrawing ligand substituents, are approximately half of the corresponding values for the catalysts 1d, 3b, and 4c, which have electron-donating ligand substituents. A rationalization of these observations is that more electron-donating ligands give a more basic nickel hydride intermediate (Scheme 1) for the heterocoupling of Ni−H and N−H to form H2. While the basicity of the py N would also be affected by these ligand substituents, the ligand electronic effects exert a stronger influence on the Ni center. Though this may seem surprising, note that for complexes 4a−c changing only the bpy ligand electronic effect leads to the same activity trend as for pyridines and has minimal effect on the pyridyl N basicity. The results are thus consistent with the notion that the electron-donating substituents make the reduced Ni more electron rich and that the subsequent hydride intermediate becomes more reactive for heterocoupling with a pyridine-attached proton. On the basis of the ligand electronic effects and second-order dependence of [H+] on catalytic rate, the heterocoupling step for hydrogen formation is proposed to be the turnover-limiting step for the catalytic cycle. This is similar to the case for the [Ni(P3N2)2]+ complexes of Dubois and co-workers.46−49 The higher activity observed for 1d and 3b relative to 1a−c and 3a, respectively, may also be due to the steric influence of the Me substituent that would facilitate dechelation as shown in Scheme 1.

A correlation between the photocatalytic and electrocatalytic activity of the nickel thiolate catalysts for hydrogen generation is also observed. For example, complex 4c is the most active catalyst for light-driven H2 generation, and it also has the most cathodic catalytic wave relative to 4b and 4a (Table 10). A similar ordering is also observed for complexes 3a,b. This fits our mechanistic model, because once the catalyst is reduced (step 3 in Scheme 1), the resultant intermediate would have a larger driving force for hydride formation and hence a faster TOF for hydrogen production from heterocoupling of the hydride and proton.

The Ni pyridinethiolate catalyst can also be generated in situ with addition of 3 equiv of the pyS−ligand to Ni(NO3)2.
Control experiments performed with Ni(NO₃)₂ or [Ni(bpy)₃]²⁻ (PF₆)₃ in the system in the absence of an N-donor ligand did not produce significant amounts of hydrogen (Figures 3b and 4). While the addition of 5 equiv of pyridine to Ni(NO₃)₂ yielded a system of modest activity (420 TON of H₂), hydrogen-generating activity increased substantially upon the addition of 1 equiv of the pyS²⁻ ligand (the ligand is added as pySH but is rapidly deprotonated under the basic reaction conditions). The activity of the system reached a maximum at 3 equiv of pyS²⁻ ligand (Figure 4), but further addition of ligand led to no further activity increases. The results highlight the importance of using the pyridinethiolate ligand for catalysis and its dual roles in stabilizing the reduced Ni center and providing a means for transferring protons from solution to a suggested hydride intermediate.

**CONCLUSIONS**

Several nickel pyridine- and pyrimidinethiolate complexes are active for both light-driven and electrocatalytic hydrogen production in aqueous/organic solvent mixtures. The initial photochemical step is reductive quenching in which the Fľľ excited state is reduced by reaction with TEA. This pathway dominates because the relative concentration of TEA is 10³ greater than that of the Ni catalyst. However, an oxidative quenching pathway can be enforced by using low TEA concentration and higher Ni catalyst concentration, leading to a system that is more robust but less active under these conditions.

The catalytic mechanism for H₂ formation at the nickel ion starts with a protonation of the pyridyl N that is likely to occur with dechelation. The protonated pyridyl N subsequently forms in the cycle for H₂ generation. The rate-limiting step is proposed to be H⁻ formation, which is fastest when electron-donating groups are used on the supporting ligands. The highest activity catalyst is 4c, which exhibits TON and TOF values that are among the highest for molecular noble-metal-free photochemical systems.

**EXPERIMENTAL SECTION**

**Materials.** The complexes ([Et₄N][Ni(pyS)₃] (1a) and [Ni(bpy)₃]²⁻ (FP₆)₃ (5) were synthesized by previously reported methods and recrystallized from acetonitrile. 1,3,5,7,8,10-Cyclooctatetraene (C₈) was used as solvent without further purification unless otherwise stated. Pyridine-2-thiol (pySH), 5-CI-pyridine-2-thiol (5-CIpySH), 5-CF₃-pyridine-2-thiol (5-CF₃pySH), 6-CH₃-pyridine-2-thiol (6-MepySH), pyrimidine-2-thiol (pySH), pyrimidine-2-thiol (pymSH), 4,6-(CH₃)₂pyrimidine-2-thiol (4,6-dmpymsH), 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmmbpy), 4,4′-dimethoxy-2,2′-bipyridine (dmobpy), nickel(II) nitrate hexahydrate, nickel(II) chloride hexahydrate, sodium metal, fluorocel (Fl), tetrahylammonium bromide (Et₄NBr), tetrahylammonium chloride (Et₄NCI), tetrahylammonium hexafluorophosphate (Bu₄NPF₆), and triethylamine (TEA) were purchased from Aldrich and used without further purification.

**Syntheses.** All syntheses of nickel thiolate complexes were performed in Schlenk flasks under an N₂ atmosphere and using solvents dried with 4 Å molecular sieves. Complexes 1a–d 2, and 3a,b were stored under N₂, and 4a–e were stored under ambient atmosphere without protection from water and oxygen.

**Spectroscopic Measurements.** ¹H and ³¹P NMR were recorded on a Bruker Avance 400 or 500 MHz spectrometer and are reported in ppm at room temperature. ¹H NMR spectra were referenced to the residual solvent peak, and ³¹P NMR spectra were referenced to trifluorotoluene. UV–vis spectra in acetonitrile were taken on a Cary 60 UV/vis spectrophotometer using a 1 cm path length quartz cuvette.

([Et₄N][Ni(5-ClpyS)₃] (1b). 5-ClpySH (0.5 g, 3.4 mmol) was added to a solution of sodium methoxide which was prepared by dissolving Na (79 mg, 3.4 mmol) in methanol (5 mL). One equivalent of Et₄NBr (0.72 g, 3.4 mmol) was added afterward. After the mixture was stirred for 1 h, the solvent was removed under vacuum. ([Et₄N][Ni(5-ClpyS)₃] was extracted with 10 mL of acetonitrile and filtered, and a solution containing ([Et₄N][Ni(5-ClpyS)₃] (0.39 g, 0.85 mmol) in 10 mL of acetonitrile was added slowly over 30 min. As the addition of the nickel precursor proceeded, the color of the solution changed from yellow to green with a white precipitate. After the mixture was stirred for 2 h, its volume was reduced to ~10 mL, causing precipitation of the green product. The mixture was later filtered and kept at ~20 °C for 24 h. The green block crystals were collected by suction filtration and dried under vacuum. The crystal yield was 0.22 g (41%) on the basis of ([Et₄N][NiCl₄]). ¹H NMR (CD₃CN, 20 °C): δ 10.55, 80, 12.1, 3.2, 1.2 ppm. Anal. Calc. for C₉H₇NiS₄Cl₄: C, 44.36; H, 4.69; N, 9.00. Found: C, 44.64; H, 4.78; N, 9.02.

([Et₄N][Ni(5-CF₃pyS)₃] (1c). This complex was prepared in a manner analogous to that described for 1b except for the purification process. After the green complex was formed and stirred for 2 h, the solvent was removed completely by vacuum. A 65 mL portion of dry diethyl ether was added to extract most of the green complex, while the white precipitate remained insoluble. The solution was filtered and the solvent was removed. The product was allowed to dry overnight under vacuum and collected as a brown powder. The yield was 0.022 g (35.6%). ³¹P¹H NMR (CD₃CN, 20 °C): δ 19.27 (s). ¹H NMR (CDCl₃): δ 104, 68.8, 12.4, 3.2, 1.2 ppm. Anal. Calc. for C₆H₇NiS₄Cl₂: C, 43.17; H, 4.04; N, 7.74. Found: C, 42.97; H, 4.02; N, 7.41.

([Et₄N][Ni(6-MepyS)₃] (1d). This complex was prepared in a manner analogous to that described for 1b. The yield was 0.31 g (65%). ¹H NMR (CD₃CN, 20 °C): δ 63.6, 54.2, 9.8, 3.2, 1.3, ~7.7 ppm. Anal. Calc. for C₁₀H₇NiS₃Cl₃: C, 55.62; H, 6.82; N, 9.98. Found: C, 55.33; H, 6.86; N, 9.94.

([Ni(hpyS)₂(5-NO₃)₂]·EtOH (1e). A 0.177 g (2.5 mmol) amount of Ni(NO₃)₂(H₂O)₆ in 5 mL of EtOH was added to a solution containing 1.11 g (10.0 mmol) of pySH in 24 mL of EtOH. A dark green precipitate appeared during addition. After 1 h of stirring, the solid product was collected through filtration. A small portion of the product that remained in the filtrate was collected as dark green crystals after keeping the solution at ~20 °C for 10 h. The combined yield was 1.23 g (73%). ¹H NMR (CD₃OD, 20 °C): δ 7.63 (4H, 8H), 6.79 (4H) ppm. Anal. Calc. for C₁₂H₁₃N₈S₃O₆Ni: C, 38.29; H, 3.21; N, 13.39. Found: C, 38.25; H, 3.25; N, 12.90.

([Et₄N][Ni(pymS)₃] (3a). PymSH (0.5 g, 4.46 mmol) was added to a solution of potassium tert-butoxide (0.5 g, 4.46 mmol) in 5 mL of methanol. Et₄NBr (0.937 g, 4.46 mmol, 1.00 equiv) was added. After the mixture was stirred for 1 h, the solvent was removed under vacuum. ([Et₄N][pymS]₃ was extracted with 10 mL of acetonitrile and filtered into a solution containing Ni(NO₃)₂(H₂O)₆ (30.7 g, 0.17 mmol) in 15 mL of acetonitrile. The color of the solution changed from blue to green during addition. After 2 h of stirring, the volume of the mixture was reduced to ~12 mL, and to this solution was added 10 mL of diethyl ether to give a white precipitate. The solution was filtered and cooled to 0 °C. Dark green crystals were collected after 24 h. The yield was 0.42 g (63%). ¹H NMR (CD₃CN, 20 °C): δ 101, 46.3, 15.5, 3.2, 1.2. Anal. Calc. for C₁₀H₉N₂S₃O₆Ni: C, 45.98; H, 5.60; N, 18.77. Found: C, 45.95; H, 5.60; N, 18.59.

([Et₄N][Ni(4,6-dmpyms)₃]·(Et₄N)Cl (3b). This complex was prepared in a manner analogous to that described for 3a except for using TEA instead of potassium tert-butoxide as base. After the volume of the solution was reduced to ~12 mL, the mixture was stored at 0 °C overnight. Clear crystals formed, and the solution was filtered. Volatile materials were removed from the filtrate to give a crude green product, which was washed with 1/20 acetonitrile/diethyl ether mixture. Green crystals were obtained by recrystallization of the crude product from 1/2 v/v acetonitrile/ether mixture at room temperature. The yield was 0.57 g (60%). ¹H NMR (CD₃CN, 20 °C): δ 44.3, 3.1, 1.3, ~7.0 ppm. Anal. Calc. for C₁₅H₁₈N₈S₃O₆Ni: C, 51.65; H, 7.72; N, 15.06. Found: C, 51.89; H, 7.51; N, 15.12.
Ni(bpy)(pyS)$_2$ (4a). This complex was originally synthesized by a electrochemical method and recrystallized with the bpy starting ligand. Here, we report a straightforward chemical method that gives pure material with high yield. A solution of 2,2'-bipyridine (1.0 g, 6.4 mmol) in 15 mL of acetonitrile was added slowly to a solution containing Ni(NO$_3$)$_2$$\cdot$$H_2$O (1.86 g, 6.4 mmol) in 100 mL of acetonitrile over 30 min. The color of the solution changed from light blue to dark blue. A solution containing pySH (1.42 g, 12.9 mmol) and TEA (2.2 mL, 16.0 mmol) in 50 mL of acetonitrile was then added slowly over 1 h. The solution turned orange, and a yellow precipitate formed after stirring for another 1 h. The product was collected by filtration and dissolved in a minimal amount of CH$_2$Cl$_2$. A layer of hexane was added slowly to the top of the solution. Dark orange needles were collected after 2 days. The yield was 2.4 g (86%).

1H NMR (CDCl$_3$, 20 °C): $\delta$ 138, 110, 72, 60.2, 57.5, 43.8, 15.8, 10.6 ppm. Anal. Calcld for C$_{20}$H$_{16}$N$_4$S$_2$Ni: C, 54.09; H, 3.63; N, 15.72; S, 11.01. Found: C, 54.38; H, 3.71; N, 15.64.

Ni(4,4'-dmdbpy)(pyS)$_2$ (4b). This complex was prepared in a manner analogous to that described for 4a. The yield was 3.3 g (93%).

1H NMR (CDCl$_3$, 20 °C): $\delta$ 110, 74.8, 58.4, 57.2, 10.7, 5.4, -9.2 ppm. Anal. Calcld for C$_{20}$H$_{16}$N$_4$S$_2$Ni-C$_3$H$_6$: C, 50.39; H, 4.05; N, 10.22. Found: C, 50.35; H, 4.00; N, 10.18.

Photolysis Setup for Hydrogen Evolution Studies. Samples in EtOH/H$_2$O (1/1; 5.0 mL) containing 4.0 μM catalyst, 2.0 mM Fl, and TEA (5% v/v) were prepared in 40 mL scintillation vials and protected from light before use. The pHs of the solutions were adjusted to pH 11.4 by adding HCl or NaOH and measured with a pH meter. The samples were placed into a temperature-controlled block at 15.0 °C and sealed with an airtight cap, and a yellow precipitate was prepared in the same solvent mixture (pH adjusted to 11.6) were added, and the intensity of the fluorescence was monitored by steady-state fluorescence, exciting at 460 nm on a Spex Fluoromax-P fluorimeter with a photomultiplier tube detector.

X-ray Diffraction Studies. Crystals were placed onto the tips of glass capillary tubes or fibers and mounted on a Bruker SMART CCD platform diffractometer for data collection. For each crystal a preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. Full data collections were carried out using Mo Kα radiation (0.71073 Å, graphite monochromator) with frame times ranging from 25 to 60 s and at a detector distance of approximately 4 cm. Randomly oriented regions of reciprocal space were surveyed: three to six major sections of frames were collected with 0.5° steps in $\omega$ at three to six different $\varphi$ settings and a detector position of $\pm$38° in $\varphi$. The intensity data were corrected for absorption. Final cell constants were calculated from the xray centroids of about 4000 strong reflections from the actual data collections after integration.

Structures were solved using SIR97 and refined using SHELXL-97. Space groups were determined on the basis of systematic absences, intensity statistics, or both. Direct-methods solutions were calculated, which provided most non-hydrogen atoms from the E map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Full-matrix least-squares refinements on $F^2$ were run to convergence.

Systems with TEA as Sacrificial Donor. When using TEA as a sacrificial donor, the net reaction being driven photochemically can be expressed by the equation

$$\text{N}_{2} \text{H}_3 + \text{H}_2 \text{O} \rightarrow \text{H}_2 + \text{HNEt} + \text{CHO}$$

Using the tabulated thermochemical data, the $\Delta F^0$ value of this reaction is calculated to be +117.6 kJ/mol. If the entropy term is dominated by the release of $H_2$, the $\Delta G^0$ value for the reaction can be estimated to be +80 kJ/mol at 15 °C. Thus, it is a thermodynamically unfavorable reaction and must be driven by light energy.

**ASSOCIATED CONTENT**

**Supporting Information**

CIF files giving X-ray structures, tables giving crystal data and structure refinement details, and figures giving UV–vis and 1H NMR spectra for nickel complexes, NMR spectra on 1a,d protons, Fl fluorescence quenching data, cyclic voltammograms of nickel complexes with addition of acid in organic solvent, and additional photocatalytic hydrogen production data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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