

Molecular Cobalt Pentapyridine Catalysts for Generating Hydrogen from Water

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 Supporting Information

ABSTRACT: A set of robust molecular cobalt catalysts for the generation of hydrogen from water is reported. The cobalt complex supported by the parent pentadentate polypyridyl ligand PY5Me₂ features high stability and activity and 100% Faradaic efficiency for the electrocatalytic production of hydrogen from neutral water, with a turnover number reaching 5.5×10^4 mol of H₂ per mole of catalyst with no loss in activity over 60 h. Control experiments establish that simple Co(II) salts, the free PY5Me₂ ligand, and an isostructural PY5Me₂ complex containing redox-inactive Zn(II) are all ineffective for this reaction. Further experiments demonstrate that the overpotential for H₂ evolution can be tuned by systematic substitutions on the ancillary PY5Me₂ scaffold, presaging opportunities to further optimize this first-generation platform by molecular design.

Growing global energy demand and concerns over climate change mediated by greenhouse gases released upon burning fossil fuels are driving the development of alternative and sustainable energy sources. Hydrogen, when derived from carbon-neutral processes, is an attractive clean fuel candidate for renewable energy storage and transport.^{1–6} In this regard, well-defined molecular catalysts, particularly those that utilize cheap and earth-abundant metals, provide an appealing approach toward H₂ production owing to the potential to understand and tune performance through chemical design. Nature has evolved iron- and/or nickel-dependent hydrogenase enzymes for producing H₂ from aqueous media with high efficiency and activity, but the large size and relative instability of these molecules under aerobic conditions present challenges for their use in artificial devices.^{7–10} Whereas many beautiful examples of H₂-evolution catalysts that mimic the inner workings of such enzymes have been developed, most require the use of organic acids and fairly negative potentials.^{11–21} In addition, abiotic earth-abundant metal complexes featuring cobalt,^{22–26} nickel,^{27–31} and molybdenum^{32,33} have been shown to generate H₂ at less extreme potentials, but many of these catalysts still utilize organic solvents, acids, and/or additives that result in organic byproducts. Thus, creating molecules for H₂ generation from water that are based upon earth-abundant elements, require no organic additives, and maintain high efficiency and activity in aqueous

media remains a significant challenge. Here, we demonstrate that a pentapyridine ligand with adjustable donor properties can provide new molecular cobalt complexes for robust, efficient, and active electrocatalytic H₂ generation from neutral pH water without organic additives.

We have initiated a program aimed at developing molecular catalysts for reactions relevant to sustainable energy cycles, with specific efforts focusing on the use of polypyridyl ancillary ligands to support reactive earth-abundant metal complexes that are stable and maintain their activity in benign aqueous media. Recently, a cobalt complex supported by the tetradentate ligand 2-bis(2-pyridyl)(methoxy)methyl-6-pyridylpyridine (PY4) was shown to catalyze the reduction of protons to H₂ in 50% aqueous media,²⁶ whereas a molybdenum-oxo complex ligated by the pentadentate platform 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine (PY5Me₂) was demonstrated to facilitate the generation of H₂ from neutral pH water or even seawater.³⁴ Encouraged by these findings and related work on biomimetic PYS oxidation chemistry,^{35–41} we reasoned that exploring first-row transition metal complexes supported by PY5Me₂ and related platforms could afford systems for reductive catalysis with aqueous compatibility.

Metalation of PY5Me₂ with Co(CF₃SO₃)₂(MeCN)₂ in acetonitrile proceeds smoothly at room temperature to afford [(PY5Me₂)Co(MeCN)](CF₃SO₃)₂ (**1**, Figure 1). Consistent with the structure of the PF₆[−] analogue,^{42–44} the Co(II) center in [(PY5Me₂)Co(MeCN)]²⁺ resides in a slightly distorted octahedral geometry with acetonitrile bound at the apical site. The cyclic voltammogram of **1** in acetonitrile solution features a reversible redox couple at $E_{1/2} = -0.83$ V vs SHE assigned to a metal-based Co(II)/Co(I) reduction, with a second irreversible reduction peak arising at -1.72 V vs SHE (Supporting Information Figure S1). A quasi-reversible oxidative wave at $+0.88$ V vs SHE can further be assigned to a Co(II)/Co(III) oxidation event. The free PY5Me₂ ligand is electrochemically silent in this potential range (Figure S2). When the cyclic voltammogram of **1** is measured in dichloromethane, the Co(II)/Co(I) reduction appears as an electrochemically irreversible peak at -0.96 V vs SHE (Figure S3).

To avoid any possible influence from acetonitrile when investigating the electrochemistry in water, the metalation of PY5Me₂ was carried also out with Co(CF₃SO₃)₂(MeCN)₂ in a 9:1 acetone/water mixture, resulting in the isolation of

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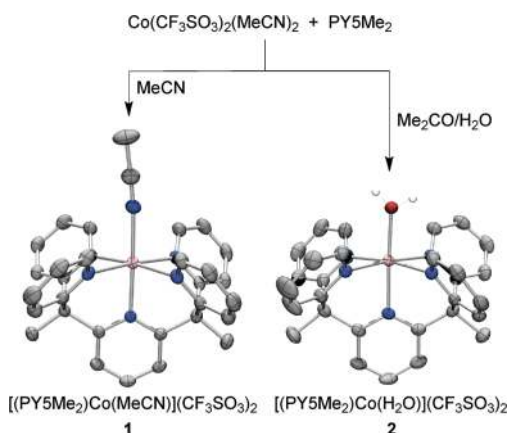


Figure 1. Synthesis of compounds **1** and **2**, and crystal structures of the complexes $[(\text{PYSMe}_2)\text{Co}(\text{MeCN})]^{2+}$ and $[(\text{PYSMe}_2)\text{Co}(\text{H}_2\text{O})]^{2+}$ with thermal ellipsoids drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): for **1**, Co–N_{PY} 2.095(3)–2.142(3), Co–N_{MeCN} 2.123(3), N_{PY}–Co–N_{PY} 80.4(1)–99.6(1), N_{PY}–Co–N_{MeCN} 91.8(1)–94.3(1); for **2**, Co–N 2.103(2)–2.150(1), Co–O 2.055(2), N–Co–N 80.83(8)–101.59(8), N–Co–O 91.12(7)–96.30(8).

$[(\text{PYSMe}_2)\text{Co}(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_2$ (**2**, Figure 1). The crystal structure of **2** confirms the expected octahedral geometry for $[(\text{PYSMe}_2)\text{Co}(\text{H}_2\text{O})]^{2+}$ with a coordinated apical water ligand. The cyclic voltammogram of **2** in dichloromethane is qualitatively similar to that observed for **1**, with the irreversible reductive peak shifted by +0.05 to –0.91 V vs SHE (Figure S4). A quasi-reversible oxidative wave is also observed at +0.93 V vs SHE with a peak shape suggestive of an electrochemical stripping process.⁴⁵ Here again, the observed features can be assigned to Co(II)/Co(I) and Co(II)/Co(III) redox changes, respectively. To check that these processes are indeed associated with metal-centered instead of ligand-based redox changes, the compound $[(\text{PYSMe}_2)\text{Zn}(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_2$ (**3**) was synthesized for comparison (see SI). The crystal structure of **3** is shown in Figure S5. The absence of any redox processes for the analogous octahedral complex of the redox-inactive Zn(II) ion within the potential window of dichloromethane (Figure S6) confirms that the ligand alone is not responsible for the redox chemistry observed for **2**.

Cyclic voltammetry experiments were performed on an aqueous solution of compound **2** maintained at pH 7 using phosphate buffer. A mercury pool electrode was employed in these measurements, owing to its low activity for water reduction and correspondingly large reductive window. For the buffered electrolyte alone, no catalytic current arises until the potential is scanned beyond –1.6 V vs SHE (Figure 2). Upon addition of **2**, however, a peak at –1.00 V vs SHE, corresponding to the Co(II)/Co(I) reduction, is followed by a sharp increase in current beginning at –1.20 V vs SHE. This rise in current, which coincides with the evolution of bubbles, can be attributed to the catalytic generation of H₂ from neutral water.³⁴ Using a controlled growth mercury drop electrode as the working electrode owing to its smaller background current, we scanned the cyclic voltammogram of **2** to more negative potentials (Figure S7). In addition to the first reduction peak at –1.00 V vs SHE, which is partially proton coupled based on the pH dependence studies (Figure S8), a second reduction peak (–1.21 V vs SHE) appears at the rise of the catalytic current and is pH independent (Figures S7 and S8). Furthermore, it was found that the catalytic current

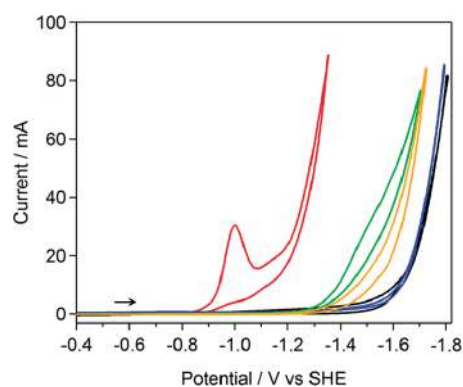


Figure 2. Cyclic voltammograms of 71 μM Co(II)-PYSMe₂ complex **2** (red), 67 μM Zn(II)-PYSMe₂ complex **3** (orange), 16 μM PYSMe₂ (green), 93 μM CoCl₂ (blue), and blank control (black) measured in aqueous solution buffered to neutral pH (1.0 M phosphate, pH 7). Only the Co(II)-PYSMe₂ complex **2** markedly lowers the overpotential for generating H₂ from water compared to the bare electrode.

maximum of **2** is dependent on catalyst concentration (Figure S9) and pH (Figure S10) but independent of scan rate (Figures S11 and 12), indicating the catalyst is functioning in a diffusion-controlled regime and is molecular in nature.

A number of control experiments were carried out to verify that $[(\text{PYSMe}_2)\text{Co}(\text{H}_2\text{O})]^{2+}$ is responsible for the catalysis. In particular, the free PYSMe₂ ligand, CoCl₂, and compound **3**, featuring the analogous complex of the redox-inactive Zn(II) ion, were each measured under identical conditions. As shown in Figure 2, the catalytic competency achieved with **2** is not matched by just PYSMe₂ or $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, as might arise from dissociation of the ligand, nor can it be accomplished with the PYSMe₂ ligand bound to a redox-inactive metal. Thus, a combination of the redox-active cobalt ion and the ancillary ligand is essential for catalytic activity.

To assess the overpotential⁴⁶ required for electrochemical production of H₂ from water in the presence of **2**, controlled potential electrolysis (CPE) experiments were performed using a custom-made double-compartment cell (Figure S13). Charge buildup at various applied potentials was monitored over the course of 1-min electrolyses performed on a 38 μM solution of **2** in water buffered at pH 7. As shown in Figure S13, the total charge consumed is negligible for overpotentials below –0.52 V and increases approximately linearly with time at more negative applied potentials. Importantly, the onset of the catalytic current occurs at an overpotential of –0.66 V (–1.07 V vs SHE), which is just slightly more negative than the Co(II)/Co(I) reduction potential.

To estimate the Faradaic efficiency for H₂ production by the catalyst, a 2-h CPE experiment was performed in a 1.0 M aqueous potassium chloride solution (Figure S14).³⁴ The evolution of H₂ during the experiment was confirmed by mass spectral analysis. For each H₂ molecule liberated, two OH[–] anions are left behind, resulting in an increase in the pH of the solutions and providing a simple means of quantifying the amount of H₂ produced. The observed rise in pH during the course of the CPE measurement closely matches that calculated based on the amount of charge consumed. The generated H₂ volume was also directly measured via gas chromatography and overlaps well with the amount calculated from consumed charge (Figure S15). The data from both methods establish that catalyst **2** operates at close to 100% Faradaic efficiency, meaning that every electron goes toward H₂ production without generation of wasteful organic byproducts.

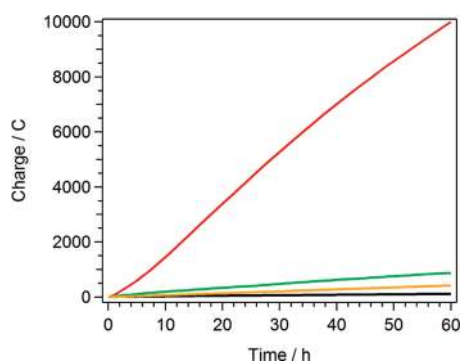


Figure 3. Extended controlled potential electrolysis of $4.7 \mu\text{M}$ Co(II)-PYSMe₂ complex **2** (red), $8.9 \mu\text{M}$ Zn(II)-PYSMe₂ complex **3** (orange), $6.2 \mu\text{M}$ PYSMe₂ (green), and blank control (black) in aqueous solution buffered to neutral pH (2.0 M phosphate, pH 7), showing charge build-up versus time with an applied potential of -1.30 V vs SHE. Only the Co(II)-PYSMe₂ complex **2** is active for generating H₂ from water.

The durability of catalyst **2** was assessed in an extended CPE experiment performed in water and maintained at pH 7 with a 2.0 M phosphate buffer. To ensure a rapid turnover rate during the electrolysis, a potential of -1.30 V vs SHE was employed for the measurement. As depicted in Figure 3, the catalyst affords a robust and essentially linear charge build-up over time, with no substantial loss in activity over the course of 60 h. Significantly, control experiments employing either the free PYSMe₂ ligand or the analogous Zn(II) compound **3** show little or no activity under the same conditions. Based on the bulk concentration of **2** ($4.7 \mu\text{M}$) used in the experiment, a turnover number (TON) of 5.5×10^4 mol of H₂ per mole of catalyst is calculated. This value is significantly greater than has been reported for other molecular cobalt catalysts for electrochemical H₂ production in neutral water.^{22–26} It is important to note that the TON obtained for **2** is a conservative underestimate, since only the small fraction of catalyst molecules interacting with the electrode are contributing to H₂ production. Indeed, a series of 12-h CPE experiments indicated that the calculated TON and associated turnover frequency (TOF) depend upon the concentration of **2** used in the experiment, with the latter reaching a maximum value of 0.3 mol of H₂ per mole of catalyst per second (Figure S16). In addition, the CPE experiment was terminated after 60 h only due to depletion of the buffer capacity at high concentrations of hydroxide ions, as we observe no degradation of the Co catalyst within this time frame. Taken together, these data establish compound **2** as a robust and active catalyst for H₂ generation from neutral water.

A key advantage of a well-defined molecular catalyst lies in the possibility of tuning its performance via synthetic chemistry. The parent [(PYSMe₂)Co(H₂O)]²⁺ is indeed a highly robust and active catalyst based upon an earth-abundant metal, but it is still necessary to lower the overpotential at which it operates. As an initial test of the tunability of this system, two new derivatives of PYSMe₂ with substituents placed at the *para* position of the central pyridine ring were synthesized (Figure 4): 4-trifluoromethyl-2,6-bis(1,1-di(pyridin-2-yl)ethyl)pyridine (CF₃PYSMe₂), featuring an electron-withdrawing CF₃ group, and 4-dimethylamino-2,6-bis(1,1-di(pyridin-2-yl)ethyl)pyridine (NMe₂PYSMe₂), featuring an electron-donating NMe₂ group. A metalation procedure directly analogous to that employed in the preparation of **2** afforded the compounds [(CF₃PYSMe₂)Co(H₂O)](CF₃SO₃)₂ (**4**) and [(NMe₂PYSMe₂)Co(CF₃SO₃)](CF₃SO₃) (**5**). Single-crystal X-ray analysis for the compounds revealed the

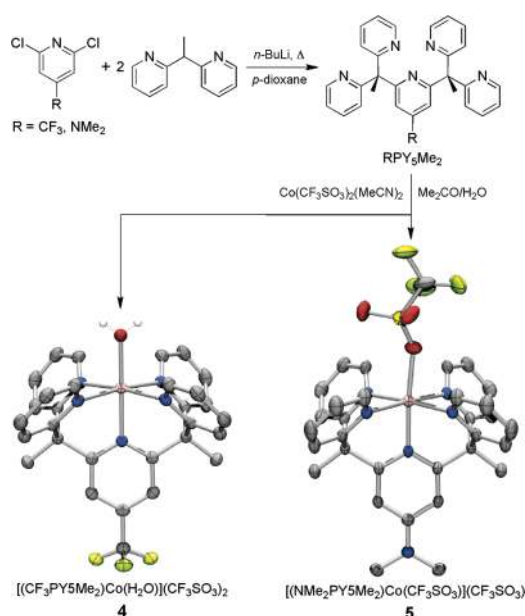


Figure 4. Syntheses of the new pentapyridine ligands RPYSMe₂ (R = CF₃, NMe₂) and compounds **4** and **5**, and the crystal structures of the resulting complexes [(CF₃PYSMe₂)Co(H₂O)]²⁺ and [(NMe₂PYSMe₂)Co(CF₃SO₃)]⁺, with thermal ellipsoids drawn at the 75% and 50% probability level, respectively. Selected interatomic distances (Å) and angles (deg) for **4** and **5**, respectively: Co–N 2.124(2)–2.133(2) and 2.065(4)–2.133(3); Co–O 2.050(3) and 2.118(5); N–Co–N 81.06(8)–98.96(8) and 81.34(10)–99.54(14); N–Co–O 92.7(1)–94.0(1) and 87.2(6)–96.9(6).

structures of the octahedral [(RPYSMe₂)CoX]ⁿ⁺ (X = H₂O and *n* = 2 for **2** and **4**, CF₃SO₃[−] and *n* = 1 for **5**) complexes to be nearly congruent. It is anticipated that the bound CF₃SO₃[−] anion in **5** will be easily replaced by a H₂O molecule when **5** is dissolved in an aqueous solution, resulting in the formation of [(NMe₂PYSMe₂)Co(H₂O)]²⁺.

Electrochemical measurements show that indeed the Co-PYSMe₂ catalyst is highly tunable, with even these substitutions on a single pyridine ring leading to significant shifts in the reduction potentials. The cyclic voltammograms of compounds **2**, **4**, and **5** in CH₂Cl₂ are compared in Figure S17. As expected, the primary Co(II)/Co(I) reduction potentials track systematically with the electronic nature of the substituent. Thus, the complex with the electron-withdrawing CF₃ group exhibits the most positive reduction potential (-0.76 vs SHE) compared to the parent complex (-0.91 vs SHE), while the congener with the electron-donating NMe₂ group is shifted to more negative potentials (-1.07 V vs SHE). As shown in Figure 5, similar shifts are apparent for experiments conducted in neutral aqueous media, with the Co(II)/Co(I) reduction peaks occurring at -0.84 , -1.00 , and -1.12 V vs SHE for **4**, **2**, and **5**, respectively (Figure S18). Most importantly, the subsequent sharp rise in current shifts in the same manner, indicating that the substitutions do in fact adjust the potential at which catalysis arises.

The foregoing results demonstrate [(PYSMe₂)Co(H₂O)]²⁺ to be an active and long-lived catalyst for the generation of hydrogen from neutral water. Significantly, peripheral substitutions on the PYSMe₂ ligand are seen to shift the potential required for catalysis in a logical manner, opening the way to the design of analogues that operate at much lower overpotentials. Future work will focus on the synthesis of variants of the

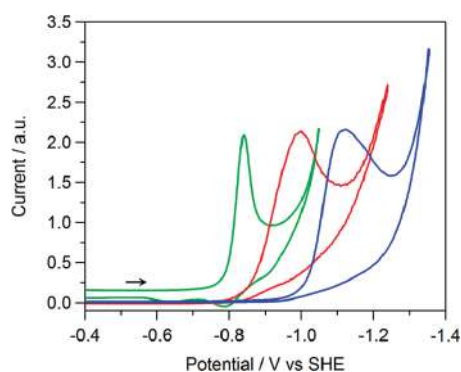


Figure 5. Normalized cyclic voltammograms of Co-PY5Me₂ derivatives, showing the parent **2** (red), CF₃-substituted **4** (green), and NMe₂-substituted **5** (blue) versions in aqueous solution maintained at pH 7 with a 1.0 M phosphate buffer.

complex bearing additional electron-withdrawing substituents, and on establishing the mechanism by which the new catalysts are functioning. Light-driven hydrogen generation by these catalysts in the presence of photosensitizers is also under investigation.

■ ASSOCIATED CONTENT

S Supporting Information. Details of syntheses and electrochemistry experiments, supporting figures, and X-ray structure information (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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