COMMUNICATION www.rsc.org/chemcomm | ChemComm

Hydrogen evolution by cobalt tetraimine catalysts adsorbed on electrode surfaces†

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Received (in Berkeley, CA, USA) 14th October 2009, Accepted 10th November 2009
First published as an Advance Article on the web 25th November 2009
DOI: 10.1039/b921559j

Aryl-substituted tetraimine complexes related to Co(dmgBF$_2$)$_2$-(MeCN)$_2$ (dmg = dimethylglyoxime) were synthesized and are active for hydrogen evolution. Co(dmgBF$_2$)$_2$(MeCN)$_2$ can be adsorbed to a glassy carbon electrode. The chemically modified electrode is active for hydrogen evolution in aqueous solution at pH < 4.5, with an overpotential of only 100 mV.

Developing efficient hydrogen evolution catalysts composed of earth-abundant materials is of considerable current interest.[1] Recent work has established that cobalt tetraimine macrocyclic complexes such as Co(dmgBF$_2$)$_2$(MeCN)$_2$ (dmg = dimethylglyoxime) (**1**)[2] can function as efficient electrocatalysts for the production of hydrogen from protons.[3–5] These systems are attractive because they operate at low overpotentials and at potentials that are quite positive relative to previously explored Co and Ni macrocycle systems. Nickel–phosphine and cobalt systems pioneered by the DuBois lab are of similar interest.[6] Because the ultimate use of such electrocatalysts in a H$_2$-evolving device will likely require grafting them to an electrode surface, we sought to ascertain whether these cobalt catalysts would still function once tethered to an electrode, and how their respective stabilities would be impacted.[7–9] Related surface studies have utilized a Nafion membrane to obtain a functional electrode–catalyst system.[10]

Derivatization of tetraimine-based macrocycles with the form of **1** is not very versatile due to the metal-templated method used in the ligand's synthesis. We have therefore examined a ligand related to a known Schiff base/oxime tetraimine construct,[11] for which the ligand can be preformed before addition of cobalt. Herein, we report that these tetraimine cobalt complexes can be used to prepare chemically modified electrodes from indium tin oxide (ITO)-coated glass that are active for hydrogen evolution. We moreover establish that **1** is a substantially better hydrogen-evolving catalyst in aqueous solution once attached to a glassy carbon (GC) electrode.

Access to various aryl-substituted tetraimine complexes related to **1** was achieved *via* a two-step synthesis involving initial isolation of the proton-linked glyoxime tetraimine followed by generation of the BF$_2$-linked analogue (see Fig. 1 for labeling scheme and ESI† for synthetic details).[12] Solid-state structures were obtained for compounds **3–6** and **8** (Fig. S1).†

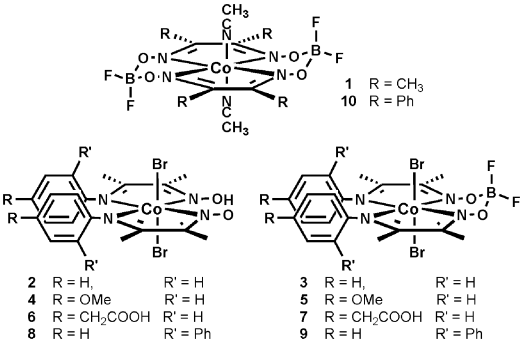

Fig. 1 Line drawings of **1–10**.

Electrochemical measurements performed on 0.1 M Bu$_4$NClO$_4$ acetonitrile solutions of **2–9** revealed a quasi-reversible Co$^{III/II}$ couple and a reversible Co$^{II/I}$ couple in each case (Table S1, ESI†). As expected, BF$_2$-linked complexes display Co$^{II/I}$ couples shifted ~200 mV anodic of the analogous H-linked complexes. In the presence of acid, electrocatalytic hydrogen evolution is observed at a potential corresponding to the Co$^{II/I}$ couple of the complexes wherein tosylate anion has replaced the bromide axial ligand (Fig. S2).† We have previously used tosic acid as a non-coordinating acid to study catalysis by **1**.[3] In the present case, binding of the TsO$^-$ anion to the Co centers occurs and shifts the electrocatalytic potential positive of the Co$^{II/I}$ couple for H-linked catalysts, and to the negative of this couple for BF$_2$-linked catalysts; this was confirmed by electrochemical experiments on **4** and **5** performed in the presence of excess Et$_4$NOTs, which resulted in analogous peak shifts (Fig. S3).† These catalysts operate with overpotentials ranging from 250 to 500 mV, and controlled potential electrolysis experiments performed in 53 mM TsOH·H$_2$O indicated approximately 75% Faradaic efficiency for the BF$_2$-linked catalysts; the H-linked catalysts are far less stable (Table S1).†

Chemically modified electrodes were prepared from the carboxylic acid-substituted derivative **7** by heating ITO-coated glass slides in an acetonitrile solution of the complex at 70 °C for 16 h.[13] Variable scan rate cyclic voltammetry experiments revealed a reversible redox couple at −0.46 V *vs.* SCE (Fig. 2a), coincident with the couple observed for **7** in solution (−0.41 V, Fig. S4).† The small peak to peak separation (E_p = 50 mV) and the linear relationship between peak current and scan rate (Fig. S5)† strongly suggest that the active redox species is adsorbed on the electrode surface.[14] The cross-sectional area of each molecule on the surface was estimated from the single crystal X-ray structure determination of **6** and yielded a theoretical coverage value of 2.0×10^{-10} mol cm^{-2}. This value assumes that

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† Electronic supplementary information (ESI) available: Syntheses and characterization of compounds, plots of electrochemical measurements, CIF files for solid-state structures. CCDC 735555–735559. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b921559j

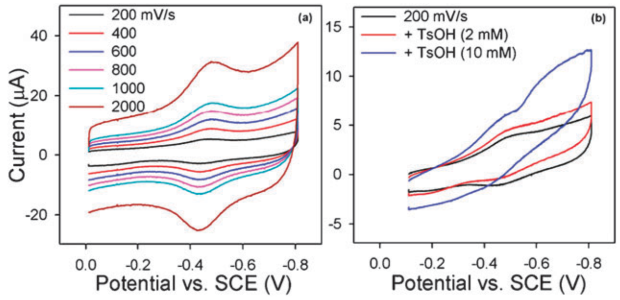

Fig. 2 (a) Scan rate dependence (0.2–2 V s^{-1}) of the current response for **7** adsorbed on ITO in 0.1 M $TBAClO_4$ MeCN solution. (b) Catalytic H^+ reduction using an ITO electrode modified with **7** in 0.1 M $TBAClO_4$ and tosic acid MeCN (scan rate 0.2 V s^{-1}).

each molecule binds through the carboxylate-appended unit. From the slope of the peak current *versus* scan rate plot a value of 1.3×10^{-10} mol cm^{-2} was determined experimentally for the surface coverage, corresponding to roughly a monolayer of catalyst.

When tosic acid (2 mM) was added, a rise in current above the $Co^{II/I}$ redox couple was evident, consistent with electrocatalytic hydrogen production (Fig. 2b). The ITO electrode could be removed from solution and rinsed with MeCN before immersion in fresh electrolyte to see that the catalyst remained bound to the surface. However, experiments involving immersion of the electrode in acid for several hours resulted in substantial leaching of the catalyst into solution.

In response to the poor stability of the ITO electrodes we have developed an alternate method for attachment of a cobalt catalyst to a GC electrode surface that is more robust. In the presence of tosic acid (53 mM), compound **1** could be adsorbed to a GC electrode surface by controlled potential electrolysis at −0.6 V for 1 h (3.1 C passed, 2 mA cm^{-2}).[15,16] CV's recorded before and after adsorption revealed a rise in current of over 100% compared with the GC electrode in solution prior to electrolysis (Fig. 3a). We presume that the implied increase in reaction rate stems from faster electron transfer to the catalyst now in contact with the electrode surface. When the electrode was removed from solution, rinsed with MeCN and reimmersed in a fresh electrolyte solution of tosic acid (0.63 mM), a catalytic wave associated with the $Co^{II/I}$ redox couple was observed (Fig. 3b). Moreover, the catalytic current remained constant for a stirred solution when the potential was held constant at −0.60 V. This indicates that under reducing conditions in the presence of acid the chemically modified electrode with compound **1** is a stable and functional hydrogen evolution catalyst in acetonitrile. When a CV of the modified electrode was recorded in MeCN solution containing 0.1 M $TBAClO_4$ and 10 mM Bu_4NOTs an irreversible wave at −0.5 V was observed (Fig. S6, ESI†), which is within 100 mV of the $Co^{II} \rightarrow Co^{I}$ reduction half-wave for complex **1** in solution. A surface coverage of 1.14×10^{-9} mol cm^{-2} was calculated from the area under this cathodic peak in a typical experiment. When the same experiment is performed in the absence of Bu_4NOTs an asymmetric stripping wave at −0.3 V is observed on the first cathodic scan (Fig. S6),† suggesting that the TsO^- anion is involved in maintaining contact of **1** to the surface in the MeCN system.[17] Attempts to attach **1** to pyrolytic graphite edge-plane (PGE) electrodes were unsuccessful. A control experiment was performed using GC and tosic acid wherein catalyst **1** was replaced by $CoBr_2$.[18] Enhancement of the catalytic current was not observed (Fig. S7).† This result, in addition to the location of the catalytic wave, coincident with the $Co^{II/I}$ potential for **1** in solution (Fig. 3b), suggests that the tetraimine complex is the active catalyst in this system.

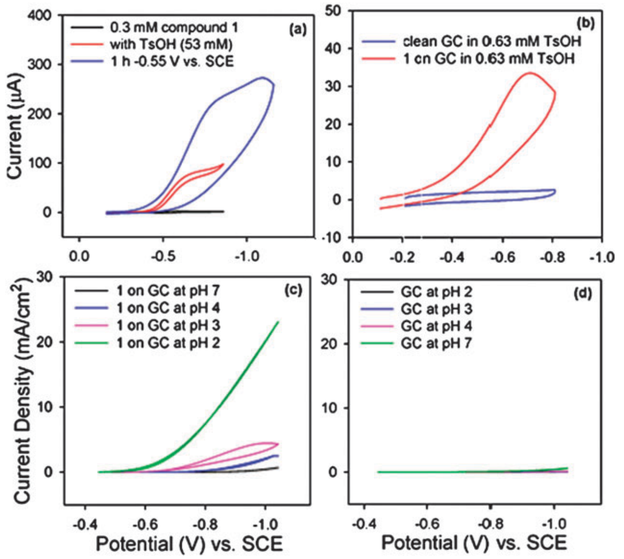

Fig. 3 (a) Catalytic H^+ reduction by **1** before (red) and after (blue) electrolysis at −0.55 V. 0.3 mM **1** in 0.1 M $TBAClO_4$ MeCN (black), (b) (blue) CV recorded with GC electrode in 0.1 M $TBAClO_4$, 0.63 mM TsOH in MeCN. (red) CV recorded with GC electrode modified with **1** in 0.1 M $TBAClO_4$, 0.63 mM TsOH in MeCN. (c) CV's recorded using a GC electrode modified with **1** in aqueous phosphate-buffered solutions at pH 2, 3, 4 and 7. (d) Control experiment with clean GC. Scan rates: 0.1 V s^{-1}.

Investigations were performed on related tetraimine cobalt catalysts that promised similar behavior. Complex **7** was assessed because carboxylic acid functional groups might be expected to yield better adsorption to the electrode surface; **3** and $Co(dpgBF_2)_2(MeCN)_2$ (**10**) were investigated because they have far lower solubility in acetonitrile, which might be expected to enhance the modified-electrode longevity. However, in all cases stable modified electrodes could not be obtained using GC or PGE electrodes: desorption was observed upon subsequent cathodic scans in 0.63 mM tosic acid solution (Fig. S8 and S9).† These observations lead us to speculate on the possibility that it is the zwitterionic nature of **1**, combined with its planar structure, that allows the charged centers to interact favorably with the GC surface.

The discussion above concerns measurements performed in acetonitrile solution using the organic acid, tosic acid. For **1** dissolved in phosphate-buffered aqueous solution at pH 7 irreversible $Co^{III/II}$ and reversible $Co^{II/I}$ redox couples are observed at 0.09 and −0.70 V *vs.* SCE, respectively, and an increase in current at −0.95 V occurs as the pH is lowered (Fig. S10).† However, bulk electrolysis experiments establish very limited hydrogen production activity suggesting degradation instead; a Faradaic yield measured at pH 4 using phosphate buffer confirmed only a 15% hydrogen yield. We therefore hoped that the GC electrode modified with **1** might exhibit enhanced catalyst stability and hence activity in aqueous solutions.[9]

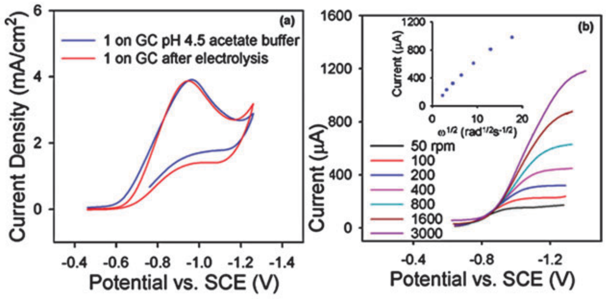

Fig. 4 CV's in 0.1 M $NaClO_4$, 2 mM NaOAc, 2 mM HOAc, pH 4.5. (a) Catalytic H^+ reduction by **1** before (blue) and after (red) electrolysis (10 mV s^{-1}). (b) Rotating disc electrode voltammetry (1 mV s^{-1}). Inset: Levich plot of limiting current at −1.2 V.

A chemically modified electrode was prepared from **1** as described above. When the modified electrode was immersed in pH 7 phosphate buffer the current barely increased above that observed when a clean GC electrode was used (Fig. 3c and d). However, as the pH was lowered from 7 to 2, the current increased by two orders of magnitude compared to the clean GC surface.[19] At the lowest pH value studied (pH 2), the onset of current increase occurred at −0.6 V, corresponding to an overpotential of 240 mV. Controlled potential electrolysis experiments performed on a stirred solution (−0.90 V, pH 2) operated with a current density of ∼1 mA cm^{-2}; the pH of the buffered solution remained constant and analysis of the headspace revealed an 80(±10)% Faradaic yield for hydrogen evolution, which remained constant for a period of more than 7 h (TON $\approx 5 \times 10^5$). These data establish that **1** retains its H_2-evolving efficacy and its stability in aqueous phosphate solution more favorably once attached to a GC electrode.

CV measurements were also performed in acetate buffered solution (Fig. 4a). In this case a peak-shaped catalytic wave was observed at −0.85 V. The onset of current increase occurred at −0.6 V corresponding to an overpotential of only 100 mV.[20] This catalysis by the modified GC electrode is coincident with the $Co^{II/I}$ couple for **1** observed in a homogeneous acetate buffered solution (Fig. S12, ESI†), providing further circumstantial evidence that **1** is the active species on the electrode. A Faradaic measurement performed in acetate buffered solution (−0.95 V, η = 400 mV) indicated a 75(±10)% H_2 yield and TON of 5×10^6;[21] the experiment operated at ∼1 mA cm^{-2} for 16 h. A CV recorded after the experiment revealed a trace identical to that collected prior to electrolysis indicating that the modified electrode remained intact (Fig. 4a). The non-linearity of the Levich plot (current *vs.* $\omega^{1/2}$, Fig. 4b) from a rotating disc electrode voltammetry experiment indicates a kinetic, rather than mass transport, limitation for the reaction under these conditions; reduction of protons must be the rate determining step since electron transfer to **1** adsorbed on GC is presumably fast.

In summary, we have introduced a synthetically versatile cobalt tetraimine system for electrocatalytic hydrogen evolution. These systems can be modified with carboxylic acid appendages and adsorbed to ITO. Similarly, the BF_2-substituted glyoximato system **1** can be adsorbed to a GC electrode upon which it is active for hydrogen evolution in aqueous solutions at low overpotential. We are currently investigating the mechanism of the immobilization of **1** on GC.

This work was supported by an NSF Center for Chemical Innovation (CHE-0802907) and by the Chesonis Family Foundation. Grants from NSF provided instrument support to the DCIF at MIT (CHE-9808061, DBI-9729592). We thank Dr Bruce Parkinson for helpful comments.

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