

Electrocatalytic H₂ production using cobaloxime complexes

Hydrogen is the most fundamental and prevailing of chemical elements in our universe. Such is its importance to our very existence that hydrogen fuels the Sun. However, in our oxygen rich environment on Earth, it is ubiquitous as its oxide form in H₂O which covers 72% of our planet. The natural photosynthetic apparatus has optimized solar driven water splitting evolving O₂ and producing the reductants ATP and NADPH for the transformation of CO₂ to energy rich C₃ sugars such as glyceraldehyde-3-phosphate in the Calvin cycle.¹ Through optimization of water splitting chemistry, via mimicking of the natural photosynthetic system, it is anticipated that hydrogen will spearhead a cleaner, greener future. Thus, the so called 'hydrogen economy' has the potential to provide tremendous environmental and economic profits, for both the petrochemical and energy sectors.²

Like fossil fuels, hydrogen can be stored as a chemical fuel or feedstock and its latent chemical energy utilized at a later stage, e.g. in a hydrogen fuel cell. Hydrogen production thus has a major advantage over other intermittent renewable resources in the energy sector such as solar, wind, wave and tidal power. Uniquely advantageous to hydrogen fuel is the fact that its only by-product upon oxidation (combustion or fuel cell electrolysis) is H₂O. If a successful hydrogen economy is to be developed enormous volumes will need to be produced to meet the global demands in both the petrochemical and energy sectors. Almost ironically, hydrogen is currently produced from fossil fuel primary energy resources. The primary goals to make a successful transition to a hydrogen economy involve

(i) development of CO₂-free hydrogen production technologies from clean or renewable energy sources

(ii) development of low-cost hydrogen storage materials

(iii) optimization of low-cost fuel cells

One of the most successful classes of molecular H₂ production transition metal catalysts are the tetraza macrocyclic cobalt series (Fig. 1).³⁻⁶ Such complexes have been utilized to explore proton reduction catalysis via chemical, electrochemical and photochemical reduction methods.

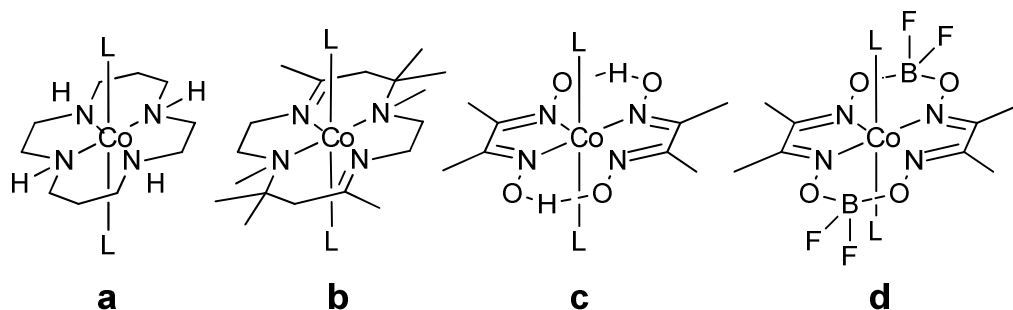
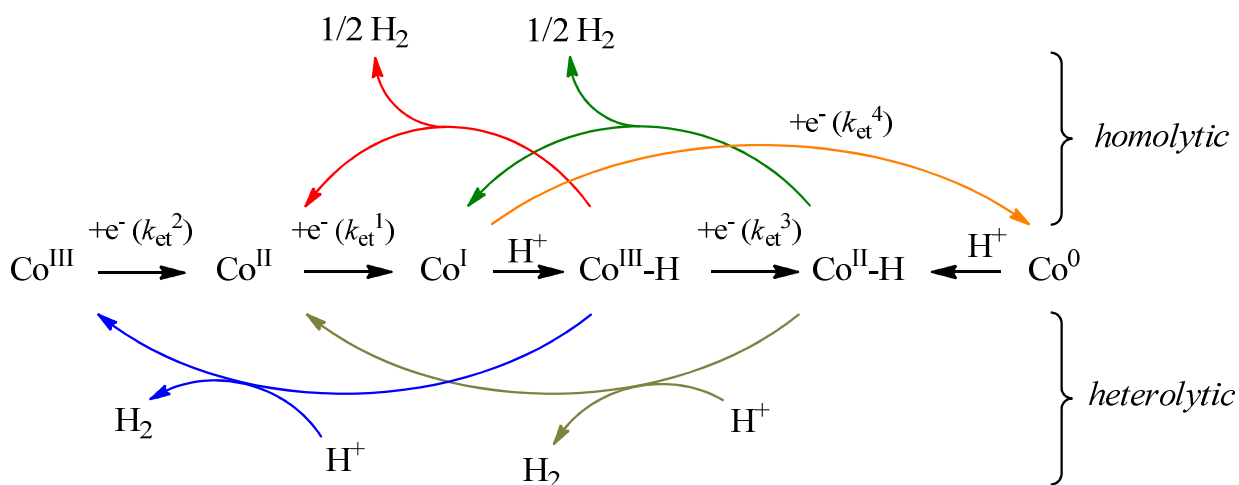


Figure 1. Structural representations of the tetraza macrocyclic cobalt H_2 production catalyst series include (a) Co-1,4,8,11-tetraazacyclodecane, (b) Co-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and (c,d) Co-glyoxime series.

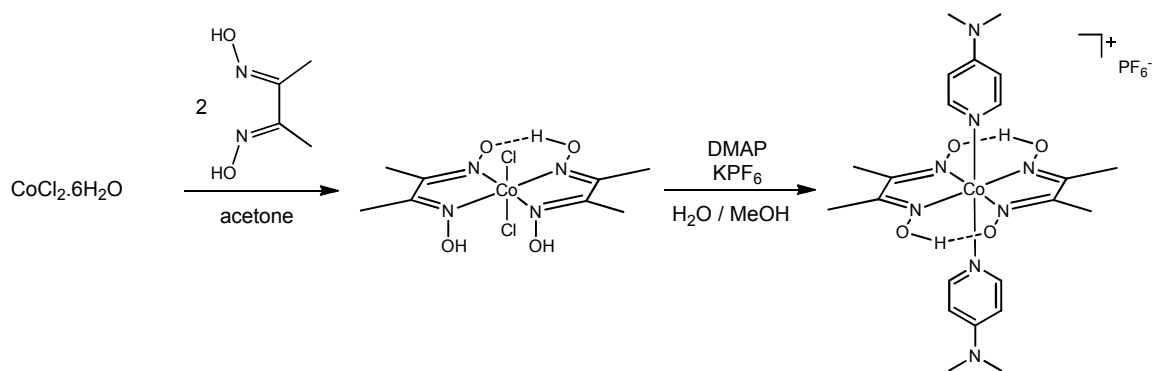
The catalytic cycle for H_2 production from cobaloximes is summarized in scheme 1. Reduction of the Co^{II} center produces a Co^{I} species that reacts with a proton source to produce a $\text{Co}^{\text{III}}\text{-H}$ complex. The $\text{Co}^{\text{III}}\text{-H}$ complex can then follow one of two pathways - homolytic or heterolytic. In the homolytic pathway a bimolecular step involving disproportionation of two $\text{Co}^{\text{III}}\text{-H}$ complexes results in H_2 evolution and two equivalents of Co^{II} . The alternate heterolytic pathway involves protonation of a single $\text{Co}^{\text{III}}\text{-H}$ site to produce H_2 and the solvated Co^{III} site.³



Scheme 1. Reaction scheme for the generation of H_2 via both homolytic and heterolytic mechanisms illustrating the pathways involved for the cobalt redox system.

Experimental

This laboratory experiment is aimed at developing your understanding of the thermodynamic and molecular processes involved in the green synthesis of H₂ gas. Although we will use electrochemistry to drive the catalysis it should be kept in mind that the cathode can be replaced with a suitable photoreductant (akin to DSSCs) thus using Solar irradiation to drive the catalytic process.^{7, 8}

**Part 1: Microscale Synthesis of $[\text{Co}^{\text{II}}(\text{dmgh})_2(\text{DMAP})_2]\text{PF}_6$**

1. To a 25-ml Erlenmeyer flask add 119 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 ml of acetone.
2. Stir vigorously to aid dissolution of the solid followed by addition of 128 mg dimethylglyoxime (dmgh_2).
3. Allow to stir until the solution becomes clear (at least 20 min) after which time a green precipitate of $\text{Co}(\text{dmgh})(\text{dmgh}_2)\text{Cl}_2$ should form.
4. Isolate the $\text{Co}(\text{dmgh})(\text{dmgh}_2)\text{Cl}_2$ intermediate by vacuum filtration. Wash with acetone.
5. Take a 5-ml reaction flask and add 50 mg of the $\text{Co}(\text{dmgh})(\text{dmgh}_2)\text{Cl}_2$ intermediate.
6. Add 2 ml of deionized H_2O followed by 0.5 ml MeOH and stir vigorously.
7. Next add 50 mg of KPF_6 salt and allow to stir for 5 min.
8. Finally add 35 mg of *N,N*-dimethyl-4-aminopyridine to generate the $[\text{Co}^{\text{II}}(\text{dmgh})_2(\text{DMAP})_2]\text{PF}_6$ product as a tan colored precipitate.
9. Isolate the solid by vacuum filtration, wash with 1 ml of water and oven dry at 80 °C for 5 min.

Part 2: Electrocatalytic H₂ production

1. Using a 0.1 M Bu₄NPF₆ electrolyte in *N,N*-dimethylformamide solvent prepare 3 ml of a 1 mM [Co^{II}(dmgH)₂(DMAP)₂]PF₆ solution.
2. Under an atmosphere of argon record a CV scan from 0 V to -1.5 V at a scan rate of 50 mV s⁻¹.
(glassy carbon working electrode, Pt-wire counter electrode and a Ag/AgCl aqueous reference electrode)
3. Maintaining an atmosphere of argon, polish the glassy carbon working electrode and record a CV scan from 0 V to -2.3 V at a scan rate of 50 mV s⁻¹.
4. Now add 1 equivalent of acetic acid (mw = 60 g mol⁻¹; d = 1.049 g ml⁻¹), polish the working electrode and repeat the CV scan from 0 V to -2.3 V at a scan rate of 50 mV s⁻¹.
5. Polishing the glassy carbon electrode in between, successively add +1, +3, +5, +10, +30, +50, + 100, +300 equivalents of acetic acid recording the catalytic current in each instance (note: potentiostat sensitivity will have to be lowered as catalytic current increases in intensity).

Laboratory Report

1. Describe synthetic steps followed and any deviations made therein. Show calculations of limiting reagents, theoretical and percentage yields.
2. Compare commercial hydrogen production methods with the electrocatalytic method here studied. Discuss the relevance of H₂ as a fuel in today's society.
3. Plot overlaid CV data with 0, 1, 5, 10, 20, 50, 100, 200, 500 equivalents of acetic acid.
4. Estimate the turnover number (TON) of the catalyst by getting the ratio of maximum catalytic current relative to the current of the same redox wave with 0 equivalents of acetic acid present.
5. Suggest a plausible mechanism for the catalytic cycle using the CV data obtained and ref 3a as a guide.

References

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