Biomimetic models of [NiFe] hydrogenase for electrocatalytic hydrogen evolution

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Chapter 6

Summary, Conclusions and Outlook

6.1 Summary

6.1.1 Introduction

The growing demand of energy indicates that global energy resources in the form of fossil fuels will not be sufficient in the future. In order to solve potential future energy problems development of a sustainable hydrogen economy is highly desirable. Researchers are looking for new and cleaner ways for the production of dihydrogen gas. The structure and function of hydrogenases have raised the attention of synthetic chemists in the past decades, since new catalysts for proton reduction may be developed by using biomimetic, functional models of hydrogenases. Three types of hydrogenases are known, being the [FeFe], [Fe] and [NiFe] hydrogenases.[1] A significant amount of data has been gathered over the years concerning the enzyme redox states and the reaction mechanism for the reversible heterolytic splitting of dihydrogen at the [NiFe] hydrogenase active site.[6] The [NiFeSe] hydrogenases form a subclass of the [NiFe] hydrogenases, in which one of the cysteines (Cys) in the active site of the enzyme is replaced by selenocysteine (Sec).[2] In the past decades a large number of structural and functional models for the active site in [NiFe] hydrogenase have been reported with overpotentials for proton reduction as low as 50 mV.[3-5] This thesis deals with the synthesis and characterization of new structural and functional models of the nickel-containing enzymes [NiFe] and [NiFeSe] hydrogenases.

6.1.2 Electrocatalytic Proton Reduction by a Model for [NiFeSe] Hydrogenases

The [NiFeSe] hydrogenase forms a subclass of the [NiFe] hydrogenases, in which one of the non-bridging cysteines (Cys) in the active site of the enzyme is replaced by selenocysteine (Sec); compared to their cysteine homologues the [NiFeSe] hydrogenases have higher catalytic activity in the hydrogen evolution reaction.[2,7-8] In Chapter 2, the synthesis and characterization is described of the two novel heterodinuclear compounds [Ni(pbSmSe)FeCpCO]PF_6 and [Ni(xbSmSe)FeCpCO]PF_6 as mimics of the [NiFeSe] hydrogenase active site. X-ray structure determinations showed that in both NiFe complexes the nickel(II) center is in a square-planar S_2Se_2 environment; the two selenolate donors are bridging to the iron(II) center that is further coordinated to an η^5-cyclopentadienyl group and a carbon monoxide ligand. The compounds show some structural similarities with the active site of [NiFeSe] hydrogenase. Electrochemical studies showed that only the complex [Ni(pbSmSe)FeCpCO]PF_6 is an electrocatalyst for the

production of H_2 in DMF in the presence of acetic acid at −2.1 V vs. Fc^+/Fc; a foot-of-the-wave (FOW) analysis of the catalytic currents yielded an estimation of k_{obs} of 24 s^{-1}.

6.1.3 Nickel-Ruthenium Based Complexes as Biomimetic Models of [NiFe] and [NiFeSe] Hydrogenases for Dihydrogen Evolution

Many ruthenium complexes are active catalysts in hydrogenation and hydrogen transfer reactions and generally ruthenium forms more stable coordination compounds than iron. Most importantly Ru(II) ions are able to accept both hard and soft ligands such as hydride and dihydrogen, which makes it suitable for replacing the Fe center in models of the [NiFe] hydrogenase.[9] In Chapter 3, the synthesis and characterization of the two nickel-ruthenium complexes $[Ni(xbSmS)RuCp(PPh_3)]PF_6$ and $[Ni(xbSmSe)RuCp(PPh_3)]PF_6$ are reported as mimics of the active site of the [NiFe] and [NiFeSe] hydrogenases. The X-ray structural analyses of the complexes show that the two NiRu complexes are isomorphous; in both NiRu complexes the nickel(II) centers are in a square-planar environment with two thioether donor atoms, and two thiolate or selenolate donors that are bridging to the ruthenium(II) center. The Ru(II) ion is further coordinated to an η^5-cyclopentadienyl group and a triphenylphosphane ligand. These complexes catalyze the dihydrogen evolution reaction in the presence of acetic acid in acetonitrile solutions at around −2.20 V vs. Fc^+/Fc with overpotentials of 810 and 830 mV. Thus they can be regarded as functional models of the [NiFe] and [NiFeSe] hydrogenases, albeit with relatively high overpotentials and rather low activity.

6.1.4 Dealkylation Through C–S and Ni–S Bond Cleavage Relevant to the Mechanism of Methyl-coenzyme M Reductase (MCR)

Nickel thiolate compounds are enjoying much attention among bioinorganic and organometallic chemists, as they are important in the context of structural and/or functional models for enzymes. Recently a number of biomimetic compounds have been reported as models for the active site in the enzymes containing a selenocysteine in their active site, in which thiolate donor atoms have been substituted by selenolates.[10,11] In Chapter 4, the syntheses are reported of the thiouronium precursor to a new chelating tetradentate dithioether-dithiolate ligand (H_2ebSmS) and the corresponding selenouronium precursor of the tetradentate dithioether-diselenolate ligand (H_2ebSmSe) as well as their nickel complexes. The complexes $[Ni_2(ebSmS)_2]$ and [Ni(pbSmSe)] were obtained, but were found to be light

sensitive and to result in partially 'decomposed' compounds upon irradiation. In all of the 'decomposed' compounds one of the alkylthiolate or alkylselenolate arms of the ligand is lost from the tetradentate ligand, resulting in dinuclear nickel(II) compounds of new asymmetric tridentate ligands. The compound [Ni(ebSmSe)] was found to be the most reactive for which only the 'decomposed' compound was obtained. The results are potentially relevant to the mechanism of action of methyl-coenzyme M reductase.

6.1.5 Synthesis and Characterization of Trinuclear [NiRu] Complexes for Electrocatalytic Proton Reduction

[NiFe] and [NiRu] complexes have been reported as structural and functional models of [NiFe] hydrogenases.[9,12,13] In Chapter 5, the synthesis and characterization are described of two new trinuclear [Ni_2Ru] complexes comprising either NiS_4 or NiS_2Se_2 complexes in order to investigate the effect of changing the sulfur donor atom to selenium on their electrocatalytic properties. The X-ray structure determinations showed that the trinuclear complex cations in [{Ni(xbSmS)}$_2$Ru(phen)$_2$](PF$_6$)$_2$ and [{Ni(xbSmSe)}$_2$Ru(phen)$_2$](PF$_6$)$_2$ contain two square-planar nickel centers bound in cis positions to the octahedral ruthenium ion via a bridging thiolate or selenolate donor atom. Electrocatalytic proton reduction occurs for both complexes in acetonitrile with addition of varying amounts of acetic acid at a potential of −2.1 V vs. Fc^+/Fc with faradaic yields of around 65%. Unexpectedly, the effect of replacing the thiolate with selenolate donor atoms appeared to be negligible.

6.2 Conclusions and Outlook

The aim of the research described in this thesis was to synthesize Ni, NiFe and NiRu complexes as mimics of [NiFe] and [NiFeSe] hydrogenases and to investigate their electrocatalytic properties for dihydrogen production. Different ligands containing thioether and thiolate or selenolate donor atoms were prepared, the synthesis and characterization of nickel complexes with these ligands were carried out and several nickel-iron and nickel-ruthenium complexes were obtained and characterized with a combination of spectroscopic techniques.

As the [NiFeSe] hydrogenases generally show higher catalytic activities than the [NiFe] hydrogenases, in the research described in this thesis the effect was studied of changing thiolate to selenolate donor atoms on the electrochemical properties and electrocatalytic activity of the molecular catalysts. Unfortunately and rather unexpectedly no significant

differences were observed, neither in the observed redox potentials and overpotential for proton reduction, nor in the electrocatalytic activity. In Chapter 2, it was shown that changing the ligand environment of the nickel center does have an influence on catalytic activity. Comparison of two related [NiFe] complexes having the same ligands bound to the iron center showed that an increased flexibility of the ligand bound to the nickel center helps to increase the catalytic activity for proton reduction. Furthermore, the interplay of two metal centers in the [NiFe] compounds seems to be beneficial for obtaining higher catalytic activity, as the separate mononuclear [Ni] and [Fe] complexes constituting the heterodinuclear [NiFe] compounds showed lower catalytic activity.

Heterodinuclear [NiRu] (Chapter 3) and heterotrinuclear [Ni_2Ru] compounds (Chapter 5) were synthesized to investigate their catalytic activity for proton reduction. Especially the [Ni_2Ru] complexes described in Chapter 5 were found to be quite stable compared to the [NiFe] complexes. Although the compound [Ni(xbSmSe)FeCpCO]PF_6 does not show catalytic activity (Chapter 2), the compound [Ni(xbSmSe)RuCp(PPh_3)]PF_6 does have catalytic activity for proton reduction (Chapter 4) which shows again the importance of second metal center and its ligand environment.

During the course of our studies to heterodinuclear model systems for hydrogenases we encountered unusual reactivity of a number of the intermediate [Ni] compounds, resulting in dealkylation of the ligands (Chapter 4). The reactivity of the compounds was found to depend on the strain of the carbon chain in the tetradentate ligand as well as the presence of either thiolate or selenolate donor groups. This reactivity not only may be of importance for the study of models for methyl-coenzyme M reductase, but also for industrial applications such as hydrodesulfurization reactions. Further exploration of this light-induced reaction with a combination of spectroscopic techniques and computational studies may shed light on the reaction pathway and pave the way toward new catalysts for desulfurisation of organosulfur derivatives.

In general, the aim of synthesizing structural mimics of the [NiFe] and [NiFeSe] hydrogenases has been successful, but unfortunately the catalytic activities of the obtained compounds are not outstanding. Although it was shown that both metal centers have influence on catalytic activity, it is assumed that the nickel center is the active site for proton reduction. In order to improve catalytic efficiency modifications are necessary for both Ni and Fe centers. A more electron-withdrawing ligand at the nickel center would help in lowering the reduction potential of the nickel ion, but on the other hand would not be beneficial for

obtaining a nickel-hydride intermediate. Further investigations thus could be directed to the design of new models in which the ligands of the iron center are substituted with electron-withdrawing groups, which may aid in lowering the reduction potential of the heterodinuclear compound without hampering formation of the nickel-hydride intermediate. Furthermore, additional proton acceptors built into the ligands for either the nickel or the iron center most likely will result in higher catalytic efficiencies.

6.3 References

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