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A (Ni–SIr)$_I$ model for [NiFe]hydrogenase

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Dedicated to Professor Georg Süss-Fink on the occasion of his 65th birthday.

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ABSTRACT

We report the synthesis and characterization of a μ-hydroxo NiRu complex as a model for the active site of (Ni–SIr)$_I$ of [NiFe]hydrogenase. This is the first example of the (Ni–SIr)$_I$ model with a bridging hydroxo ligand between dimetal centers and an available coordination site on Ni center *cis* to the bridging hydroxo ligand. We have determined the structure of the (Ni–SIr)$_I$ model complex by X-ray analysis and reported reversible switching between the catalytically inactive (Ni–SIr)$_I$ and a catalytically active (Ni–SIr)$_{II}$ models.

Introduction

[NiFe]hydrogenase ([NiFe]H_2ase) catalyzes reversible activation of H_2 into $2H^+$ and $2e^-$ *via* heterolytic cleavage of H_2 [1]. The active site of [NiFe]H_2ase provides two possible H_2-coordination sites, X and Y as shown in Fig. 1 [1g]. Which of these sites is responsible for binding to H_2, however, remains a matter of controversy [1].

Based on our previous model studies, we have proposed that the X position is the key site for H_2 activation [2,3]. The principle evidence for binding to the Y site comes from a crystal structure of [NiFe]H_2ase which bears a CO ligand at the Y position [4]. Since CO is known to deactivate [NiFe]H_2ase, it is thought that the coordinated CO ligand must therefore indicate the H_2 binding site.

The principle problem with this latter interpretation, however, is that (Ni–SIr)$_I$ (EPR-silent ready state I) bears a vacant Y site but is catalytically inactive toward H_2 (Fig. 2) [1,5]. When the X site is made available by protonation of the OH^- ligand to a labile H_2O ligand {(Ni–SIr)$_{II}$ (EPR-silent ready state II)}, H_2 activation is enabled [1,6]. The catalytically active (Ni–SIr)$_{II}$ is an unobservable intermediate with two available coordination sites (H_2O and Y). The (Ni–SIr)$_{II}$ releases H_2O to afford Ni-SIa (EPR-silent active state). The Ni-SIa is reactive toward H_2, which has two available coordination sites (X and Y).

In view of this controversy, we felt in important to construct a structurally accurate model of (Ni–SIr)$_I$ and investigate its properties. Here, we report a NiRu complex as the first example of a (Ni–SIr)$_I$ model complex, $[Ni^{II}L(NO_3)(\mu\text{-}OH)Ru^{II}(\eta^6\text{-}C_6Me_6)]$ (**1**, L = *N*,*N*′-dimethyl-3,7-diazanonane-1,9-dithiolato), with a bridging OH^- ligand between dimetal centers and an available coordination site on Ni center *cis* to the OH^- ligand [7,8], and demonstrate which X or Y coordination sites is necessary for H_2 activation.

Results and discussion

The μ-hydroxo $Ni^{II}Ru^{II}$ complex **1** as a model for (Ni–SIr)$_I$ was produced from deprotonation of an aqua $Ni^{II}Ru^{II}$ complex, $[Ni^{II}LRu^{II}(H_2O)(\eta^6\text{-}C_6Me_6)](NO_3)_2$ {[**2**]$(NO_3)_2$} as a model for (Ni–SIr)$_{II}$ [2b], in H_2O. The deprotonation process was followed by means of a titration experiment to establish the pK_a value of the H_2O ligand. Complex **2** was dissolved in H_2O and titrated with 100 mM NaOH/H_2O under an N_2 atmosphere (Fig. 3). This titration shows that the pK_a value is 8.5 ± 0.1 and the change is reversible [3b,9]. Although the pK_a value of (Ni–SIr)$_I$ has been reported as 7.8 ± 0.1, it has not been conclusively established whether a bridging cysteine or OH^- is protonated at this pH [10].

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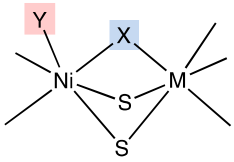

Fig. 1. Possible coordination sites, X (blue-shaded area) and Y (red-shaded area), of active site of [NiFe]H_2ase (M = Fe, X = H_2O, OH^-, or vacant coordination site and Y = vacant coordination site as shown in Fig. 2) and our models (M = Ru, X = H_2O or OH^- and Y = NO_3^-). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The structure of **1** was characterized by X-ray analysis (Fig. 4) as well as electrospray ionization-mass spectrometry (ESI-MS) and X-ray photoelectron (XP) and EPR spectroscopy (Figs. S1–S3).

The framework of **1** is based around a NiS_2Ru butterfly core bridged by the OH^- ligand (Fig. 4). The Ni atom adopts distorted octahedral coordination that is drastically changed by deprotonation of the H_2O ligand of **2**. One of the *N*-donor of N_2S_2 ligand, previously occupying the equatorial plane, moved to an axial

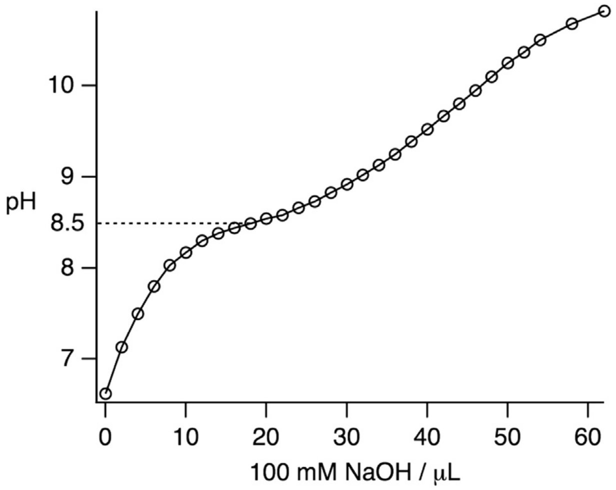

Fig. 3. pH titration of **2** (5.0 mM, 1.0 mL) with 100 mM NaOH/H_2O in H_2O under an N_2 atmosphere.

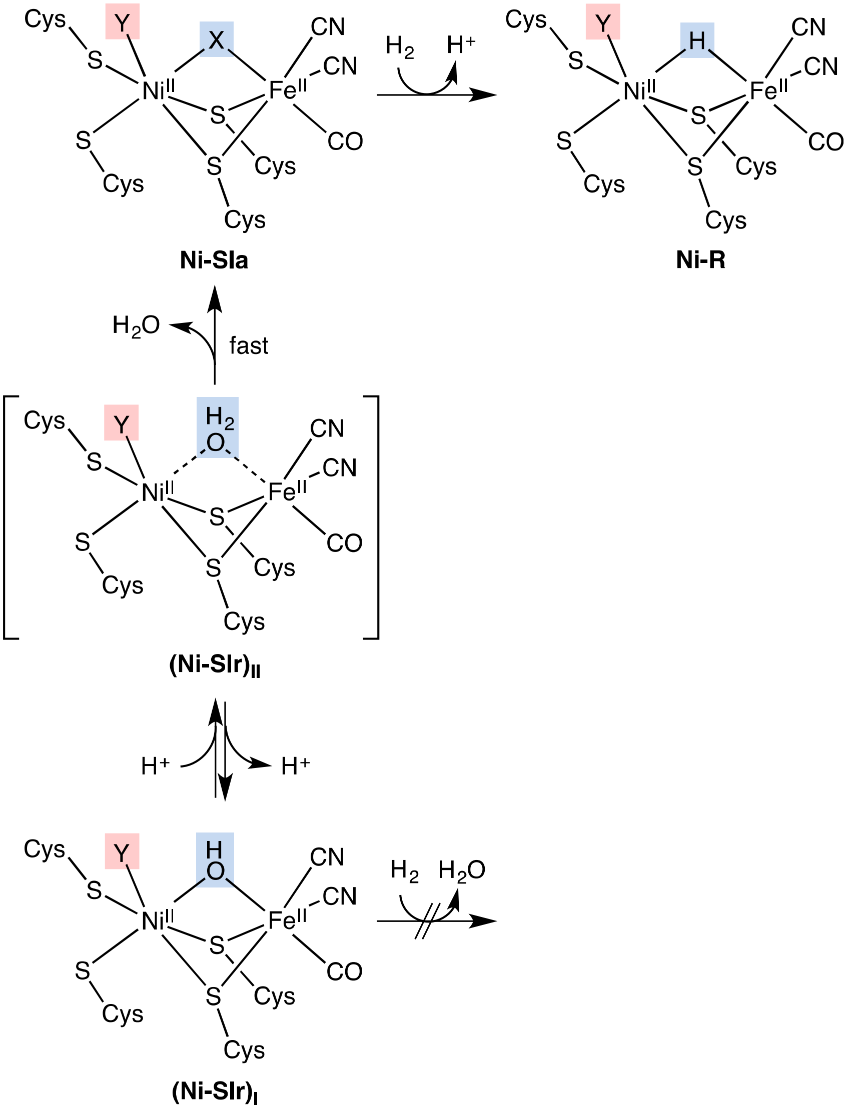

Fig. 2. Schematic representation of Ni–SIr (EPR-silent ready state), Ni-SIa (EPR-silent active state), and Ni-R (EPR-silent reduced state) of [NiFe]H_2ase. X (blue-shaded area) and Y (red-shaded area) = vacant coordination sites. $(Ni–SIr)_I$ is unreactive toward H_2, which has one available coordination site (Y). $(Ni–SIr)_{II}$ is unobservable, which has two available coordination sites (H_2O and Y). Ni-SIa is reactive toward H_2, which has two available coordination sites (X and Y). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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