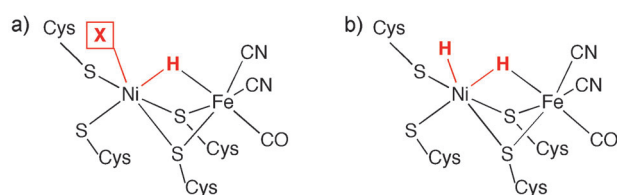


Preparation and Reactivity of a Nickel Dihydride Complex**

Takahiro Matsumoto, Takuma Nagahama, Jaeheung Cho, Takuhiro Hizume, Masatatsu Suzuki,* and Seiji Ogo*

Hydrogen has the potential to provide clean, green energy for the 21st century.^[1] One path to using hydrogen as an energy source is to develop catalysts based on the hydrogenase (H_2 ase) class of enzymes.^[2–5] In order to better understand and harness the properties of H_2 ase, we previously constructed a robust H_2 ase mimic based on a NiRu bis- μ -thiolato assembly.^[6] In addition to successfully replicating the chemical features of the $[NiFe]H_2$ ase, we were able to gain a number of crucial insights into their structural and mechanistic features. These findings have now been incorporated into the biological literature (Scheme 1).^[7]

As part of our model study, we proposed the existence of a crucial bimetallic NiRu dihydride intermediate in the catalytic cycle.^[6] Unfortunately, the dihydride could not be directly observed, but implicated by isotope labeling experiments. To provide further insights into the nature of the



Scheme 1. Proposed active-site structures of the active forms of $[NiFe]H_2$ ase. a) Monohydride active form.^[2,3c] X = vacant coordination site. b) Dihydride active form.^[7]

dihydride species, which is capable of acting as an electron donor, we have developed a remarkable dinuclear octahedral bis(μ -hydrido)dinickel(II) complex $[Ni^{II}_2(Me_2-tpa)_2(\mu-H)_2]Y_2$ (**1** Y_2 , Me_2-tpa = bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine, $Y = NO_3, BF_4$, or PF_6). Complex **1**(NO_3)₂ can be derived from the reaction of a mononuclear complex $[Ni^{II}(Me_2-tpa)(NO_3)](NO_3)$ (**2**(NO_3)) with $NaBH_4$ in H_2O . Complex **2**(NO_3) was synthesized by the reaction of $Ni^{II}-(NO_3)_2 \cdot 6H_2O$ with Me_2-tpa in CH_3CN . The structure of **2** was characterized by X-ray analysis (Figure S1 in the Supporting Information), electrospray ionization mass spectrometry (ESI-MS; Figure S2), and IR spectroscopy (Figure S3).

We investigated the dinuclear complex **1**²⁺ by X-ray analysis and describe herein the first octahedral Ni^{II} dihydride complex reported to date (Figure 1).^[8] Brown crystals of **1**(BF_4)₂ suitable for X-ray diffraction were obtained from the substitution of NO_3^- in **1**(NO_3)₂ to BF_4^- in CH_3OH at $-40^\circ C$. Complex **1** has a diamond $[Ni^{II}_2(\mu-H)_2]$ core, in which the Ni atom adopts a distorted-octahedral coordination. The average bond lengths of $Ni1-N2$ and $Ni1-N3$ (2.189 Å) are longer than those of $Ni1-N1$ and $Ni1-N4$ (2.087 Å) because of the steric requirement of the 6-methyl groups bound to the pyridines. The distance of $Ni1 \cdots Ni1^*$ (2.6105(8) Å) is longer than that of a previously reported four-coordinated Ni^{II} dihydride complex (2.3939(6) Å).^[8a]

Magnetic susceptibility measurements of **1**²⁺ in the solid state indicate the presence of an antiferromagnetic exchange interaction between two Ni^{II} centers. This interaction is also confirmed by ESR silence and signals in the diamagnetic region of 1H NMR spectrum.

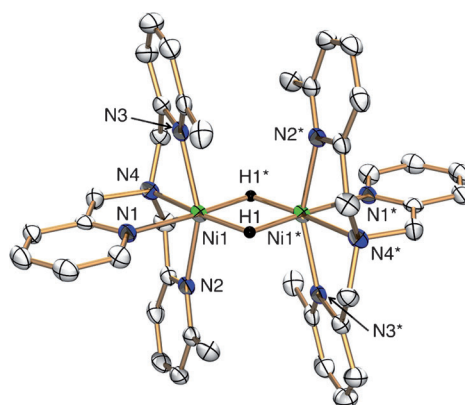


Figure 1. ORTEP drawing of **1**(BF_4)₂ with ellipsoids at 50% probability. The counteranions, solvents (CH_3OH and H_2O), and hydrogen atoms of Me_2-tpa are omitted for clarity. Selected distances [Å]: $Ni1 \cdots Ni1^*$ 2.6105(8), $Ni1-N1$ 2.075(3), $Ni1-N2$ 2.191(4), $Ni1-N3$ 2.186(4), $Ni1-N4$ 2.098(4).

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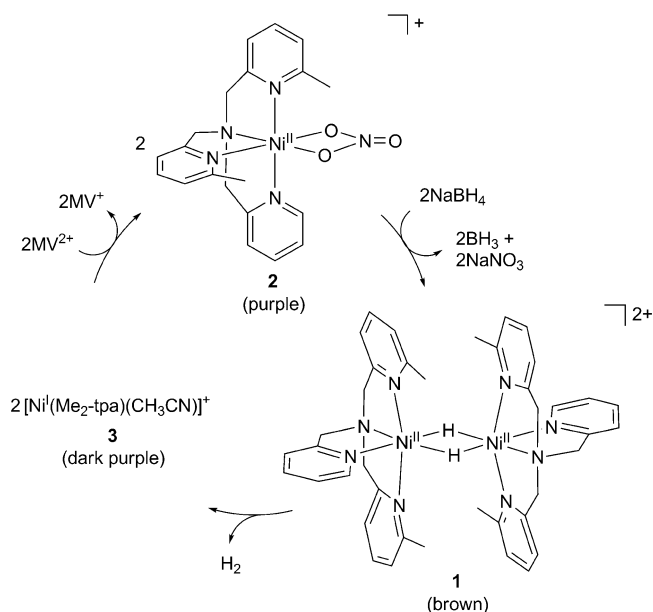
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The positive-ion ESI mass spectrum of $\mathbf{1}(\text{PF}_6)_2$ in CH_3OH shows a prominent signal at m/z 377.1 that corresponds to $\mathbf{1}^{2+}$, and a characteristic isotopic distribution that matches the calculated isotopic distribution (Figure S4 in the Supporting Information), thus indicating that $\mathbf{1}^{2+}$ has a dimeric structure in CH_3OH . To establish the origin of the hydrido ligands of $\mathbf{1}^{2+}$, $[\text{Ni}^{\text{II}}_2(\text{Me}_2\text{-tpa})_2(\mu\text{-D})_2](\text{PF}_6)_2$ ($[\text{D}_2]\text{-}\mathbf{1}(\text{PF}_6)_2$) was synthesized from NaBD_4 . The mass spectrum showed the parent peak at m/z 378.1, thus demonstrating that the hydrido ligands originate from NaBD_4 .

Of particular note is the observation that $\mathbf{1}^{2+}$ decomposes via reductive elimination to produce H_2 gas and leaves behind a low-valent Ni^{I} complex $\mathbf{3}$ in CH_3CN (Scheme 2). This decomposition is analogous to that proposed for the reductive elimination of H_2 from our NiRu model complex.^[6]



Scheme 2. Proposed mechanism for the reaction cycle with the Ni($\text{Me}_2\text{-tpa}$) complexes $\mathbf{1}$ – $\mathbf{3}$. The structures of $\mathbf{1}$ and $\mathbf{2}$ were determined by X-ray analysis. Complex $\mathbf{3}$ was characterized by ESR.

When $\mathbf{1}^{2+}$ was dissolved in CH_3CN under an N_2 atmosphere, the appearance of a strong absorption band around 590 nm, which corresponds to a gradual color change from brown to dark purple, was observed in the UV/Vis spectrum (Figure S5a,b in the Supporting Information). This color change is concurrent with the evolution of H_2 gas, where the yield of evolved H_2 is 94% based on $\mathbf{1}^{2+}$, as determined by GC. Use of $[\text{D}_2]\text{-}\mathbf{1}^{2+}$ confirmed that the H_2 originated from the hydrido ligands. The dark-purple species $\mathbf{3}$ showed an ESR spectrum typical of Ni^{I} (Figure S6 in the Supporting Information). The ESR spectrum of a frozen solution of $\mathbf{3}$ in CH_3CN , measured at 7 K, exhibits a rhombic signal with g values of 2.28, 2.16, and 2.04, which are similar to those observed for some Ni^{I} complexes.^[9]

The mechanism of reductive elimination was determined by means of products analysis of mixtures of $\mathbf{1}^{2+}$ and $[\text{D}_2]\text{-}\mathbf{1}^{2+}$. Mixing $\mathbf{1}^{2+}$ and $[\text{D}_2]\text{-}\mathbf{1}^{2+}$ in CH_3CN results in intermolecular

H^+/D^+ exchange to produce $\mathbf{1}^{2+}$, $[\text{Ni}^{\text{II}}_2(\text{Me}_2\text{-tpa})_2(\mu\text{-H})(\mu\text{-D})]^{2+}$ ($[\text{D}]\text{-}\mathbf{1}^{2+}$), and $[\text{D}_2]\text{-}\mathbf{1}^{2+}$, as confirmed by ESI-MS. These three complexes can thereafter release the corresponding gas by means of intramolecular reductive elimination to give H_2 , HD , and D_2 , as determined by GC. The evidence for intramolecular reductive elimination was supported by the fact that decomposition of $\mathbf{1}^{2+}$ to $\mathbf{3}^+$ with evolution of H_2 followed first-order kinetics ($k_{\text{H}} = 1.0 \times 10^{-3} \text{ s}^{-1}$; Figure S5c,d in the Supporting Information). Furthermore, the kinetic deuterium isotope effect value ($k_{\text{H}}/k_{\text{D}}$) was determined to be 2.4, which is consistent with that of reductive elimination of H_2 by the other metal hydride complex.^[10]

We were also able to demonstrate that $\mathbf{3}^+$ acted as a reducing agent, in common with the reduced form of our NiRu H_2 ase mimic. Complex $\mathbf{3}^+$ was able to reduce methyl viologen (MV^{2+}), the ferrocenium ion ($[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_5)_2]^+$), and methylene blue. The quantitative reduction of MV^{2+} by $\mathbf{3}^+$ in CH_3CN under an N_2 atmosphere gave MV^+ , as confirmed by UV/Vis spectroscopy (Figure S7). To the best of our knowledge, this is the first example of reduction of MV^{2+} by electrons from a metal hydride complex.^[11] A cyclic voltammogram (CV) of $\mathbf{3}^+$ in CH_3CN showed a reversible redox couple at $E_{1/2} = -1.28 \text{ V}$ versus Ag/AgNO_3 , which was assigned to the one-electron oxidation of the Ni^{I} to the Ni^{II} state (Figure S8).

Following these observations, we propose the following mechanism for the extraction of electrons from the nickel complexes (Scheme 2). In the first step, reaction of $\mathbf{2}$ with NaBH_4 produces the bis(μ -hydride) species $\mathbf{1}^{2+}$. This dihydride then undergoes reductive elimination to produce the low-valent Ni^{I} species $\mathbf{3}^+$. Complex $\mathbf{3}^+$ then reduces an electron acceptor to return to $\mathbf{2}^+$. We believe this is a mechanistic analogue for our NiRu H_2 ase mimic and, by extension, for $[\text{NiFe}]\text{H}_2$ ase itself.

In conclusion, we have synthesized a Ni^{II} dihydride complex as a model for the dihydride active form of our $[\text{NiFe}]\text{H}_2$ ase mimic. While this complex is not a direct model for the core of hydrogenase itself, it mimics many of the essential structural and mechanistic aspects, that is, it involves a dihydride complex of an octahedral Ni center, which can evolve H_2 by reductive elimination. Rather than being the complete solution, this model provides us with a central piece of evidence and we can anticipate finally solving how $[\text{NiFe}]\text{H}_2$ ase uses hydrogen as an energy source.

Experimental Section

$[\text{Ni}^{\text{II}}_2(\text{Me}_2\text{-tpa})_2(\mu\text{-H})_2](\text{PF}_6)_2$ ($\mathbf{1}(\text{PF}_6)_2$): Method A: NaBH_4 (38 mg, 1.0 mmol) was added to an aqueous solution (4.0 mL) of $\mathbf{2}(\text{NO}_3)_2$ (0.10 g, 0.20 mmol) to precipitate a brown powder of $\mathbf{1}(\text{NO}_3)_2$, which was collected by filtration. A solution of NH_4PF_6 (164 mg, 1.0 mmol) in CH_3OH (4.0 mL) was added to a solution of $\mathbf{1}(\text{NO}_3)_2$ in CH_3OH (20 mL) and the resulting mixture was allowed to stand for 3 days at -40°C to afford crystals of $\mathbf{1}(\text{PF}_6)_2$, which were collected by filtration and dried in vacuo (yield: 40% based on $\mathbf{2}(\text{NO}_3)_2$). Method B: NaBH_4 (38 mg, 1.0 mmol) was added to a solution of $\mathbf{2}(\text{NO}_3)_2$ (0.10 g, 0.20 mmol) in CH_3OH (20 mL) to give a brown solution, to which was added NH_4PF_6 (164 mg, 1.0 mmol) in CH_3OH (4.0 mL). The resulting solution was allowed to stand for 3 days at -40°C to afford brown crystals of $\mathbf{1}(\text{PF}_6)_2$, which were collected by filtration and dried

in vacuo (yield: 50% based on **2**(NO₃)). ESI-MS (CH₃OH): *m/z* (% in the range *m/z* 200–2000): 377.1 (100) [**1**²⁺], 899.3 (16) [**1**(PF₆)⁺]; elemental analysis calcd (%) for C₄₀H₄₆N₈F₁₂Ni₂P₂ (**1**(PF₆)₂): C 45.92, H, 4.43; N 10.71; found: C 46.02, H 4.21, N 10.56.

[Ni^{II}(Me₂-tpa)(NO₃)](NO₃) (**2**(NO₃)): Ni^{II}(NO₃)₂·6H₂O (0.87 g, 3.0 mmol) was added to a solution of Me₂-tpa (1.0 g, 3.1 mmol) in CH₃CN (80 mL) to give a purple solution, to which diethyl ether (200 mL) was added. The resulting solution was allowed to stand for 3 days to afford purple crystals of **2**(NO₃), which were collected by filtration and dried in vacuo (yield: 83% based on Ni^{II}(NO₃)₂·6H₂O). ESI-MS (CH₃CN): *m/z* (% in the range *m/z* 200–2000): 438.1 (100) [**2**⁺]; FT-IR (KBr disk): $\tilde{\nu}$ = 2873–3077 (m, aliphatic C–H), 1607 (s, aromatic C=C), 1576 (s, aromatic C=C), 1281–1496 cm^{−1} (m, NO₃[−]); elemental analysis calcd (%) for C₁₉H₂₂N₆NiO₇ (**2**(NO₃)·H₂O): C 46.27, H 4.66, N 16.19; found: C 46.12, H 4.62, N 16.10.

[Ni^I(Me₂-tpa)(CH₃CN)](PF₆) (**3**(PF₆)): **1**(PF₆)₂ (10 mg, 9.6 μmol) was dissolved in CH₃CN (1.0 mL) and the resulting solution was allowed to stand for 3 h to give a dark-purple solution of **3**(PF₆) with evolution of H₂. The solvent of the dark purple-solution was removed under reduced pressure to leave a dark purple powder of **3**(PF₆), which is very air- and moisture-sensitive (yield: 99% based on **1**(PF₆)₂). UV/Vis (CH₃CN): λ_{max} (ε) = 670 (3540), 347 (2640); elemental analysis calcd (%) for C₂₂H₂₅N₃F₆NiP (**3**(PF₆)): C 46.92, H 4.47, N 12.44; found: C 46.82, H 4.11, N 12.36.

X-ray crystallographic analysis: Crystals of **1**(BF₄)₂ suitable for X-ray diffraction were prepared by substituting of the NO₃[−] counterion in **1**(NO₃)₂ with BF₄[−] by adding a solution of NaBF₄ in CH₃OH to a solution of **1**(NO₃)₂ in CH₃OH at −40°C. Crystals of **2**(NO₃) suitable for X-ray diffraction were prepared by recrystallization from an CH₃CN/diethyl ether solution of **2**(NO₃). Measurements were made on a Rigaku/MSC Saturn CCD diffractometer with confocal monochromated MoK α radiation (λ = 0.7107 Å). Data were collected and processed using the CrystalClear program (Rigaku). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. CCDC 825133 (**1**(BF₄)₂) and 825134 (**2**(NO₃)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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