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[11] Data of the crystal structure of $\mathbf{8}\cdot 2\,C_6H_{14}$: $C_{124}H_{140}N_8Ni_2\cdot 4\,C_6H_{14}$, $M_r = 2204.63$, crystal from $CHCl_3/C_6H_{14}$, crystal dimensions $0.2\times 0.3\times 0.25$ mm, space group $P\bar{1}$, $a = 14.807(1)$, $b = 15.293(1)$, $c = 16.595(1)$ Å, $\alpha = 68.256(4)$, $\beta = 77.287(5)$, $\gamma = 75.368(5)^\circ$, $V = 3344$ Å^3, $Z = 1$, $\rho_{calcd} = 1.09$ g cm^{-3}; $\mu_{Mo} = 3.23$ cm^{-1}; $\theta_{max} = 27.5^\circ$. For 11 968 reflections measured; $R_1 = 0.093$ for 8446 data [$I > 3\sigma(I)$], $wR_2 = 0.114$ for all measured data. Diffraction data were collected on a Mac Science DIP-2020K imaging plate system diffractometer (105 K, $Mo_{K\alpha}$ radiation $\lambda = 0.71069$ Å). The structure was solved by direct methods and refined by F^2 with all observed reflections. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to calculated positions. Programs used: structure determination with SIR92 and refined with teXane for Windows. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133210. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] In this case, *meso*-chlorinated product was not obtained. A possible mechanism for the *meso*-bromination may be bromine-atom abstraction by a metalloporphyrin *meso*-radical, since the only available bromine source is BAHA.

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[16] After submission of this paper, we became aware that the analogous doubly *meso*-β-linked diporphyrin without chlorine subsitution at *meso*-position was formed in the reaction of **1** with $TeCl_4$: K. Sugiura, T. Matsumoto, S. Ohkouchi, Y. Naitoh, T. Kawai, Y. Takai, K. Ushiroda, Y. Sakata, *Chem. Common.* **1999**, 1957.

[Ni(NHP*n*Pr$_3$)('S$_3$')], the First Nickel Thiolate Complex Modeling the Nickel Cysteinate Site and Reactivity of [NiFe] Hydrogenase**

Dieter Sellmann,* Franz Geipel, and Matthias Moll

Dedicated to Professor Gerhard Fritz on the occasion of his 80th birthday

Hydrogenases assume a central role in the natural hydrogen and energy metabolism by catalyzing the reaction (1a). The characteristic feature of H_2 activation by hydrogenases is the heterolytic H_2 cleavage according to Equation (1b). It is established by the H_2/D^+ exchange [Eq. (1c)], and serves as test reaction for hydrogenase activity.[1]

$$H_2 \rightleftarrows 2H^+ + 2e^- \quad (1a)$$

$$H_2 \rightleftarrows H^+ + H^- \quad (1b)$$

$$D_2O + H_2 \rightleftarrows HD + HDO \quad (1c)$$

The molecular structures of a [NiFe][2] and recently also that of a [FeFe] hydrogenase[3] have been determined by X-ray crystallography. However, the mechanisms of reactions (1a)–(1c) remained discussed controversially, in particular with regard to the role and oxidation states of the metals in the active centers.[4] Figure 1 schematically depicts the active center of the [NiFe] hydrogenase from *D. Gigas* in the oxidized (inactive) form.

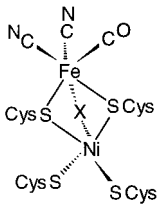

Figure 1. Schematical drawing of the active center of [NiFe] hydrogenase from *D. Gigas* in the oxidized form ("X" = O^{2-}, OH^-, H_2O).[2a]

Since the discovery of nickel as essential metal of [NiFe] hydrogenases,[5] the nickel sulfur entity of their active centers has attracted particular attention. Redox titrations, EPR, IR, and EXAFS results indicated it as the H_2 activation site. The redox processes of [NiFe] hydrogenases were interpreted either as nickel-centered comprising oxidation states ranging from Ni^{III} to Ni^0,[1] or as nickel thiolate centered yielding nickel thiyl species.[6] Alternatively, it was recently postulated that the redox processes are centered at the iron atom which is electronically coupled to nickel in the oxidation state Ni^I.[4a, 7]

Nickel complexes with hydrogenase activity are extremely rare. So far, catalysis of a H_2/D^+ exchange could be observed only with the thiosemicarbazone complex $[NiL_2]Cl_2$ (L = o-$C_6H_4(OH)$–CH=N–$NHCSNH_2$).[8] Model complexes with nickel thiolate cores and catalysis activity for the H_2

[*] Prof. Dr. D. Sellmann, Dipl.-Chem. F. Geipel, Dr. M. Moll
Institut für Anorganische Chemie
Universität Erlangen-Nürnberg
Egerlandstrasse 1, 91058 Erlangen (Germany)
Fax: (+49) 9131-8527-367
E-mail: sellmann@anorganik.chemie.uni-erlangen.de

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heterolysis have remained unknown inspite of intensive research.[9] Such complexes could solve the important question, which requirements must be met in order to achieve a heterolytic H_2 activation.

The reactions of [Ni(NHP*n*Pr$_3$)('S$_3$')] (**1a**) ['S$_3$'$^{2-}$ = bis(2-sulfanylphenyl)sulfide(2 −)][10] yielded answers to this question. Complex **1a** is diamagnetic in the solid state and in solution, has a four-coordinate Ni^{II} center surrounded by one N, one thioether, and two thiolate donors, and exhibits a strongly flattened tetrahedral coordination geometry. Figure 2 depicts the molecular structure determined by X-ray crystallography.[10]

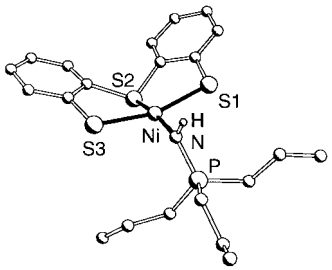


Figure 2. Molecular structure of **1a** (C-bonded H atoms omitted).

When treated with D_2 at slightly elevated pressure (10 bar), complex **1a** gave the DNP*n*Pr$_3$ complex **1b** and HD [Eq. (2)].

$$[Ni(NHPnPr_3)('S_3')] + D_2 \rightarrow [Ni(NDPnPr_3)('S_3')] + HD \quad (2)$$

The reaction is slow and could be monitored by $^1H/^2H$ NMR spectroscopy. The ^2H NMR spectrum of the reaction solution (CH_2Cl_2) showed the ND signal of **1b** at $\delta = -1.85$ after 96 h. Running the reaction (2) under 30 bar D_2 in a high-pressure NMR tube allowed the observation of the second product HD, which gives rise to a 1:1:1 triplet in the ^1H NMR spectrum (Figure 3).

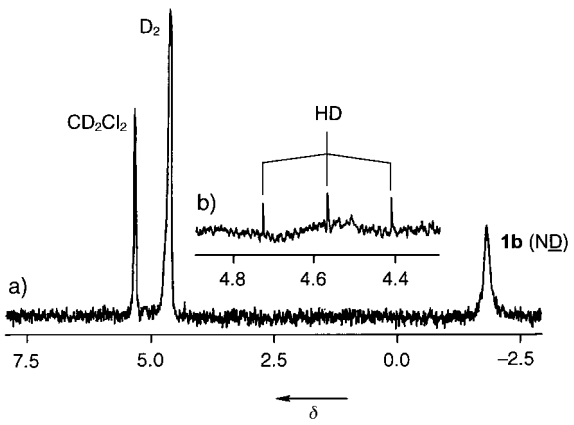


Figure 3. a) ^2H NMR spectrum of the solution of **1a** in CH_2Cl_2 under D_2 (10 bar), recorded at standard pressure after 96 h. b) HD region of the CD_2Cl_2 reaction solution when **1a** had been treated with D_2 at 30 bar for 96 h.

Removal of all volatiles yielded solid **1b**. Its IR spectrum (KBr) exhibited a ν(ND) band at 2427 cm^{-1} that could be assigned through comparison with the ν(NH) band of **1a** at 3273 cm^{-1} ($\tilde{\nu}$(NH): $\tilde{\nu}$(ND) = 1.35).

The NH proton of **1a** is weakly acidic, as demonstrated by the H^+/D^+ exchange according to Equation (3).

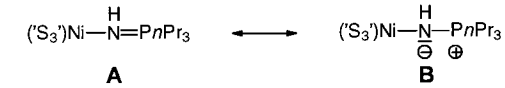
$$\mathbf{1a} + D_2O \xrightarrow{CD_2Cl_2} \mathbf{1b} + HDO \quad (3)$$

Preliminary experiments showed that the homologous [M(NHP*n*Pr$_3$)('S$_3$')] complexes with M = Pd^{II}, Pt^{II} undergo identical reactions [Eq. (2) and (3)], but are more active giving rise to shorter reaction times.

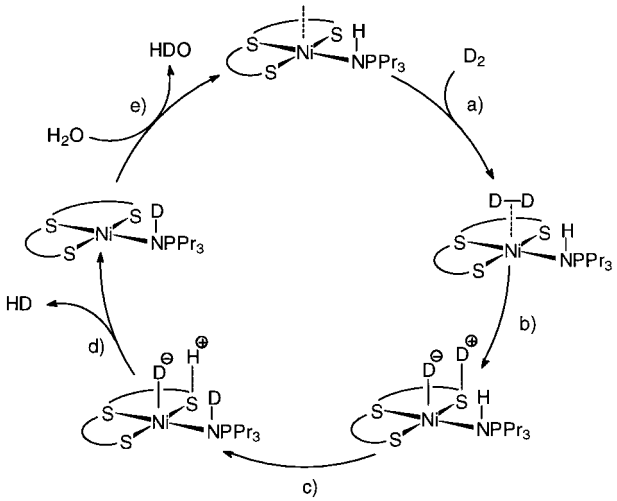
The Equations (2) and (3) demonstrate that **1a** is able to exchange NH protons with molecular D_2 and (subsequently) with H^+ or D^+. Substitution of D_2 for H_2 and combination of Equations (2) and (3) sums up to give Equation (4), which demonstrates that **1a** catalyzes the hydrogenase reaction (1c) and the heterolytic cleavage of H_2 (D_2).

$$D_2O + H_2 \xrightarrow{1a} HD + HDO \quad (4)$$

Complex **1a** contains a four-coordinate Ni^{II} center, which potentially can add one or two more ligands. In addition, complex **1a** has two built-in Brønsted basic sites represented by the thiolate-donor lone pairs. A third Brønsted basic site potentially is the N donor of the HNP*n*Pr$_3$ ligand when it assumes the phosphonium imide structure **B**.[10]



These considerations, supported by previous results on the H_2 activation at transition metal thiolate sites,[11] suggest the mechanism outlined in Scheme 1 for the D_2 heterolysis catalyzed by **1a**.



Scheme 1. Mechanism of the [Ni(NHP*n*Pr$_3$)('S$_3$')] catalyzed D_2/H^+ exchange according to Equation (1c).

D_2 adds to the nickel center (step a) and is heterolytically cleaved by the concerted action of the Lewis acidic nickel center and one Brønsted basic thiolate donor (step b). The resulting acidic thiol deuteron scrambles with the acidic phosphorane imine proton (step c). The thiol proton and nickel deuteride ligand combine to give HD, which is released (step d as reversal of steps a and b). The resulting DNP*n*Pr$_3$ complex **1b** can exchange with H_2O to give back the starting catalyst **1a** (step e).

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The results reported here allow a series of conclusions:

1) Identification and isolation of *both* the reaction products **1b** and HD enabled the unambiguous proof of the D_2 heterolysis by complex **1a**. Therefore, the HNP*n*Pr$_3$ ligand of **1a** becomes an important probe for the reaction mechanism. Furthermore, H_2/D_2 exchange reactions catalyzed homolytically by metal traces, reaction flask walls, etc. can be excluded.
2) The H_2 heterolysis catalyzed by [NiFe] hydrogenases can take place at a Ni^{II} center coordinated by cysteinate ligands. It does *not* require a $Ni^{II} \rightarrow Ni^{I}$ reduction. It requires only the removal of the "X" ligand ("X" = O^{2-}, OH^-, or H_2O) when the inactive oxidized form of [NiFe] hydrogenase is (reductively) converted into the active form.
3) The [NiS_4] geometry in Figure 1 is neither tetrahedral nor planar, but strongly distorted. The same holds true for the [$NiNS_3$] geometry of **1a**. The symmetry of four-coordinate Ni^{II} complexes, however, strongly influences the relative energies of nickel acceptor and donor orbitals that must interact with the σ and σ^* orbitals of H_2.[12] Thus it could be the asymmetry of the nickel sites in [NiFe] hydrogenase and **1a** that favors their interaction with H_2.

Experimental Section

All manipulations were carried out under exclusion of air.

D_2/NH exchange of **1a** with D_2 and identification of **1b**: In a NMR tube, a purple solution of **1a** (45 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) was treated with D_2 (10 bar) in an autoclave. ^{2}H NMR spectra were recorded after 48 and 96 h at standard pressure. After removal of all volatiles, the purple residue was identified as **1b** by IR spectroscopy.

D_2/NH exchange of **1a** with D_2 and identification of HD: The reaction of **1a** with D_2 under 30 bar was carried out in CD_2Cl_2 in a high-pressure NMR tube (Fa. Wilmad, 528-PV-1, inner diameter 2.2 mm) and monitored by ^{1}H NMR spectroscopy after 48 h and 96 h.

D^+/NH exchange of **1a** with D_2O and identification of **1b**: To a saturated solution of **1a** in CD_2Cl_2, a 50-fold excess of D_2O was added. The reaction was monitored by ^{1}H NMR spectroscopy by the decrease of the νNH signal of **1a**. The resulting **1b** was precipitated from the solution by addition of *n*-hexane and identified by its IR spectrum in KBr.

1a: ^{1}H NMR (269.6 MHz, CD_2Cl_2): $\delta = 7.50$ (d, 2H; C_6H_4), 7.28 (d, 2H; C_6H_4), 7.06 (m, 2H; C_6H_4), 6.92 (m, 2H; C_6H_4), 1.94 (m, 6H; PCH_2), 1.69 (m, 6H; CH_2), 1.05 (t, 9H; CH_3), −1.85 (s, br, 1H; NH); IR (KBr): $\tilde{\nu}$(NH) = 3273 cm^{-1}. **1b**: ^{2}H NMR (61.25 MHz, CH_2Cl_2): $\delta = -1.85$ (s, br, 1D; ND); IR (KBr): $\tilde{\nu}$(ND) = 2427 cm^{-1}.

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