

Electrocatalytic production of hydrogen by a synthetic model of [NiFe] hydrogenases

Alessandro Perra, E. Stephen Davies, Jason R. Hyde, Qiang Wang, Jonathan McMaster* and Martin Schröder*

Received (in Cambridge, UK) 23rd November 2005, Accepted 1st February 2006

First published as an Advance Article on the web 10th February 2006

DOI: 10.1039/b516613f

The radical cluster anion $[\text{Ni}(\text{L})\text{Fe}_2(\text{CO})_6]^-$ catalyses the reduction of protons to produce molecular hydrogen.

Hydrogenases are enzymes that catalyse reversibly the oxidation of dihydrogen. Their high rate of turnover (*ca.* 9000 ToN s^{-1}) makes them attractive as biocatalysts for the production of dihydrogen or as electrocatalysts in biofuel cells.¹ X-ray crystallography has confirmed that the [NiFe] hydrogenases involve a binuclear $[(\text{Cys})_2\text{Ni}(\mu\text{-Cys})_2\text{Fe}(\text{CN})_2(\text{CO})]$ core at their active sites in which the Ni centre possesses a distorted NiS_4 tetrahedral geometry (Fig. 1).² At least three redox states of the [NiFe] hydrogenases (Ni-SI_a, Ni-C, Ni-R) are believed to participate in the catalytic cycle and it is proposed that the Ni centre shuttles between formal Ni^{III} and Ni^{II} states, whilst the Fe centre remains at the formal Fe^I level.^{3,4} Illumination of the Ni-C state at temperatures below 100 K gives a new species, Ni-L, that contains a formal Ni^I centre and which converts back to Ni-C on warming.^{4,5} In general, [NiFe] hydrogenases catalyse dihydrogen consumption although activity ratios of up to 250 : 1 for dihydrogen evolution to dihydrogen uptake have been observed for *P. furiosus*.⁶

The syntheses of catalysts for the production of dihydrogen have focused on analogues of the [Fe]-only hydrogenases. These analogues catalyse dihydrogen production at very negative potentials *ca.* -1.75 to -1.91 V vs. NHE for $(\mu\text{-pdt})[\text{Fe}(\text{CO})_2(\text{X})_2]$ [$\text{pdt}^{2-} = \text{SCH}_2\text{CH}_2\text{CH}_2\text{S}^-$; X = CO or phosphine] in acetonitrile with 6–30 ToN h^{-1} .⁷ The proposed mechanisms of catalysis involve the Fe^I-Fe^I, Fe^I-Fe⁰ and Fe⁰-Fe⁰ states and proceed *via* sequential electron transfer and proton binding events that occur in a sequence that is dependent on the nature of X.^{7,8} In contrast, synthetic analogues of the active sites of the [NiFe] hydrogenases⁹ are rarely active towards dihydrogen production¹⁰ and electrocatalysis has only been observed for mononuclear Ni complexes.^{11,12} The proposed ECEC mechanisms for these

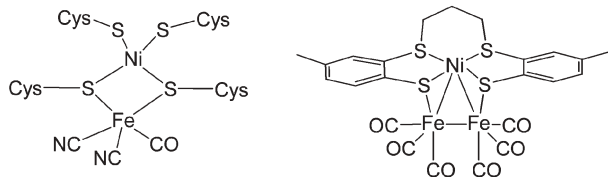


Fig. 1 Schematic view of the active site of the [NiFe] hydrogenases (left) and the complex $[\text{Ni}(\text{L})\text{Fe}_2(\text{CO})_6]$ (**1**); $[\text{L}]^{2-} = (\text{CH}_3\text{C}_6\text{H}_3\text{S}_2)_2(\text{CH}_2)_3^{2-}$.

School of Chemistry, The University of Nottingham, Nottingham, UK NG7 2RD. E-mail: m.schröder@nottingham.ac.uk; Fax: +44 (0)115 9513490; Tel: +44 (0)115 9513563

reactions involve a metal- or ligand-based reduction process, the oxidative addition of H^+ to form a $\text{Ni}^{\text{III}}\text{-H}^+$ centre and a second reduction process to a formal $\text{Ni}^{\text{II}}\text{-H}^-$ state followed by protonation to release dihydrogen.^{11–13} We have reported recently¹⁴ the synthesis and spectroscopic characterisation of the trinuclear $[\text{Ni}(\text{L})\text{Fe}_2(\text{CO})_6]$ cluster (**1**) as an analogue of the active site of [NiFe] hydrogenase. Herein, we show that **1** catalyses the production of dihydrogen in an electrochemical cell.

Complex **1** exhibits an electrochemically reversible one-electron reduction at $E_{1/2} = -1.31$ V vs. Fc^+/Fc (Fig. 2c) to generate paramagnetic $\mathbf{1}^-$. The addition of trifluoroacetic acid (TFA) to a solution of **1** in CH_2Cl_2 generates large cathodic current responses and depresses the anodic wave in the cyclic voltammogram of the test solution (Fig. 2d). The depression of the return wave is consistent with the removal of $\mathbf{1}^-$ from the diffusion layer by a mechanism other than heterogeneous electron transfer. This observation is confirmed by a plot of normalised cathodic current,

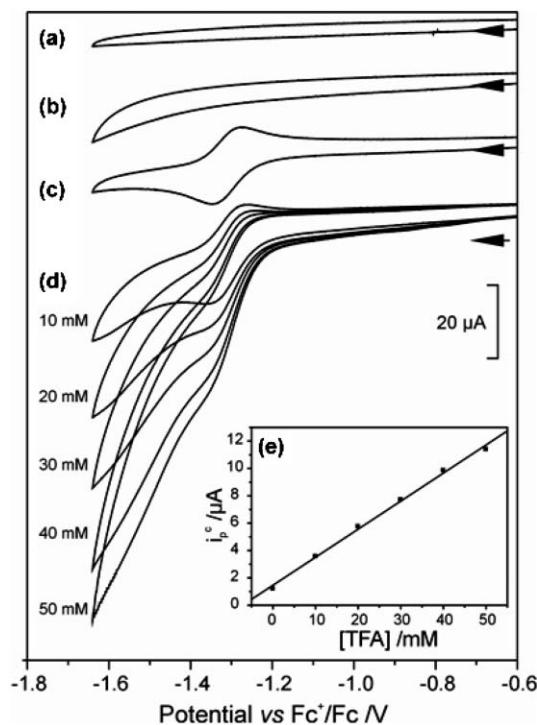


Fig. 2 Cyclic voltammograms of (a): CH_2Cl_2 and $[\text{Bu}_4\text{N}][\text{BF}_4]$ (0.4 M) as supporting electrolyte, at a sweep rate of 100 mV s^{-1} and at RT; (b): (a) + 50 mM TFA; (c): (a) + **1** (1 mM); (d): (c) + TFA at concentrations of 10, 20, 30, 40 and 50 mM. (e) Plot of i_p^c vs. [TFA] for (c) and (d).

$i_p^c v^{-1/2}$, versus the scan rate, v , (10 to 300 mV s^{-1}) (Fig. 3). The increase in $i_p^c v^{-1/2}$ with decreasing v for **1** in the presence of 50 mM of TFA is diagnostic of a catalytic mechanism involving an irreversible chemical reaction that follows a reversible charge transfer.¹⁵ In addition, the cathodic current is directly proportional to the concentration of TFA over the range 0–50 mM (Fig. 2e). In the presence of tetrabutylammonium trifluoroacetate, **1** shows a reversible cyclic voltammogram and no catalytic current. Thus, **1** is reduced reversibly to generate $\mathbf{1}^-$, which subsequently reacts with H^+ .

The products of the catalytic half-cycle were confirmed by the addition of 1.1 equivalents of TFA to a solution of electrochemically-generated $\mathbf{1}^-$. Gas chromatography confirmed the production of dihydrogen and solution IR and UV/vis spectroscopies† demonstrated the quantitative oxidation of $\mathbf{1}^-$ to **1**. In addition the IR spectrum of $\mathbf{1}^-$ remained unperturbed upon addition of an excess of tetrabutylammonium trifluoroacetate.

An assessment of the electrocatalytic activity of **1** (1 mM solution in CH_2Cl_2) was made by coulometry. The experiment was performed in an H-type cell equipped with a glassy carbon rod working electrode ($A = 182 \text{ mm}^2$) separated by a glass frit from a carbon foam counter electrode. **1** consumed an average of $13 \text{ e mol}^{-1} \text{ h}^{-1}$ in the presence of TFA (50 mM) at an applied potential of $-1.64 \text{ V vs. Fc}^+/\text{Fc}$. This corresponds to 6 ToN h^{-1} after subtraction of the background electrolysis of TFA, *ca.* 0.6 ToN h^{-1} , at this potential. The rate of electrolysis of **1** in the presence of TFA (50 mM) is *ca.* nine-fold greater than that of a solution of TFA (50 mM) alone. The depletion of H^+ in the test solution resulted in a decrease from the initial rate; however, this rate was recovered upon the addition of TFA to the test solution. In addition, a steady catalytic current could be maintained for periods up to *ca.* 1 h. Continued electrolysis resulted in a slow decolourisation of the reaction mixture due to decomposition of **1**. The neutralisation of residual TFA by Et_3N in this experiment gave the original reversible cyclic voltammogram of $\mathbf{1}/\mathbf{1}^-$.

The homogeneous nature of the catalytic process was confirmed by cyclic voltammetric and coulometric experiments. After a 5 min period of electrolysis of TFA in the presence of **1**, replacement of the test solution with a solution deficient in **1** gave a minimal current response (*ca.* 5% of the catalytic current), confirming that catalysis of the reduction of H^+ is associated with the $\mathbf{1}^{0/-1}$ couple

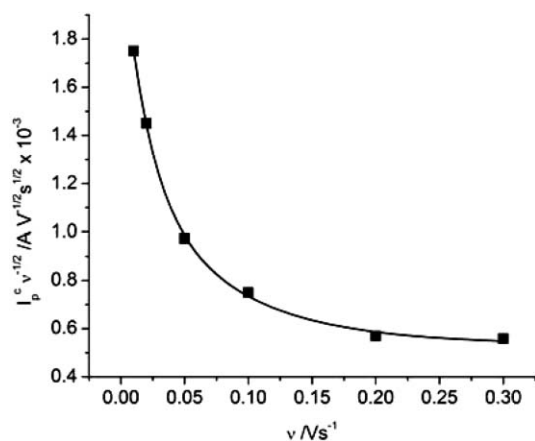


Fig. 3 Plot of $i_p^c v^{-1/2}$ vs. v for a solution of **1** (1 mM) and TFA (50 mM) in CH_2Cl_2 solution containing $[\text{tBu}_4\text{N}][\text{BF}_4]$ (0.4 M).

in solution rather than heterogeneous coverage of the electrode with decomposed **1**.

The robust nature of **1** over a period of 1 h in a 50 mM solution of TFA was established by UV/vis and IR spectroscopies in CH_2Cl_2 and by $^1\text{H-NMR}$ spectroscopy in CDCl_3 . In each case, the spectrum of **1** was unperturbed by the presence of acid, indicating that **1** does not interact appreciably with H^+ and that the protonation of **1** in the catalytic cycle is unlikely. These observations, together with the electrocatalytic behaviour of **1**, point to the binding and subsequent reduction of H^+ at the $\mathbf{1}^-$ oxidation level.

Our spectroscopic and DFT studies of $\mathbf{1}^-$ reveal an in-plane delocalised SOMO that is antibonding with respect to the metal-metal bonds within the NiFe_2 framework.¹⁴ The Ni, Fe1 and Fe2 characters (24.0, 17.1 and 16.4%, respectively) and the small thioether and thiolate S-donor contributions (2.8 and 1.4–1.7%, respectively) to the SOMO in $\mathbf{1}^-$ indicate that the protonation site is likely to be metal- and not S-based. The relatively low S-character derived from the bridging S-thiolate donors in the SOMO of $\mathbf{1}^-$ contrasts with the electronic structures of the Ni-A, -B, -C and -L states of the $[\text{NiFe}]$ hydrogenases. Within these forms a significant fraction (*ca.* 24–34%) of the spin density is at the Cys553 S atom,¹⁶ suggesting that S-redox non-innocence and S-atom protonation, rather than solely metal-based events, may play a role in the catalytic cycle of the $[\text{NiFe}]$ hydrogenases.

Protonation across a formal $\text{Fe}^{\text{I}}-\text{Fe}^{\text{I}}$ bond has been demonstrated for the complexes $(\mu\text{-pdt})[\text{Fe}^{\text{I}}(\text{CO})_2(\text{X})]_2$ ^{7,8} and the protonation of mononuclear $\text{Ni}^{\text{I}}\text{N}_2\text{S}_2$ ¹² and $\text{Ni}^{\text{I}}\text{NP}_2\text{S}_2$ ¹³ macrocyclic complexes has been implied in the mechanisms of dihydrogen production by these compounds. These observations provide further support for a metal centred protonation event in the catalytic cycle of **1** involving the Fe–Fe and/or the Ni–Fe bonds of $\mathbf{1}^-$; however, the precise mechanism for the reduction process and the formal changes in oxidation state(s) during catalysis still remain to be defined. Nevertheless, we can rule out an EECC mechanism, based on the electrochemical behaviour of **1**. This mechanism has been proposed for $(\mu\text{-pdt})[\text{Fe}^{\text{I}}(\text{CO})_3]_2$ that catalyses the production of dihydrogen at potentials beyond its *second* redox couple;⁷ **1** catalyses dihydrogen production at the *first* (and only) reduction event within the solvent window. ECCE and ECEC mechanisms involving formal $\text{Fe}^{\text{II}}-\text{H}^-$ and $\text{Ni}^{\text{III}}-\text{H}^-$ species have been proposed in the electrocatalytic cycles of $(\mu\text{-X})[\text{Fe}^{\text{I}}(\text{CO})_2\text{PMe}_3]_2$ ($\text{X} = (\text{SEt})_2, \text{edt}, \text{pdt}, \text{xyldt}$)⁷ and NiN_2S_2 macrocyclic complexes,¹² respectively. Thus, it is likely that similar intermediates and mechanisms are relevant to the electrocatalytic cycle of **1**.

The electrocatalytic production of dihydrogen by **1** occurs at similar potentials to those for NiN_2S_2 macrocyclic complexes ($E_{1/2} = -0.43$ to -0.78 V vs. NHE ; -0.83 to $-1.18 \text{ V vs. Fc}^+/\text{Fc}$)¹² but at potentials that are *ca.* 900 mV more positive than those of $(\text{X})[\text{Fe}^{\text{I}}(\text{CO})_2\text{PMe}_3]_2$ [$\text{X} = 2\text{EtS}^-, \text{edt}^{2-}, \text{pdt}^{2-}, \text{xyldt}^{2-}$; *e.g.* $(\mu\text{-pdt})[\text{Fe}^{\text{I}}(\text{CO})_2\text{PMe}_3]_2$, $E_{1/2} = -1.85 \text{ V vs. NHE}$; $-2.25 \text{ V vs. Fc}^+/\text{Fc}$]⁷ and at comparable rates of turnover (*ca.* 6–30 ToN h^{-1}). Thus, our catalytic studies on **1** demonstrate, for the first time, that a heteronuclear Ni–Fe cluster, containing biologically relevant ligands, can support the catalytic production of dihydrogen at comparable rates of turnover to those of current analogues of the active sites of the $[\text{Fe}]$ -only hydrogenases. Furthermore, **1** catalyses the production of dihydrogen at potentials that are considerably

more positive (ca. 900 mV) than $(\mu\text{-pdt})[\text{Fe}^{\text{I}}(\text{CO})_2\text{L}]_2$ and which lie close to the potential window of the $\text{Ni}^{\text{II/I}}$ couples of mononuclear NiN_2S_2 macrocyclic complexes.

We thank the BBSRC, EPSRC and the University of Nottingham for funding. MS gratefully acknowledges the receipt of a Royal Society Wolfson Research Merit Award, and of a Leverhulme Trust Senior Research Fellowship.

Notes and references

† IR (ν_{CO} , CH_2Cl_2) for **1**: 1955 (s, br), 1995 (vs), 2035 (vs); I^- : 1888 (s, br), 1922 (vs), 1967 (vs). UV/vis: $\lambda_{\text{max}}(\epsilon)$ for **1**: 359 (16700), 420 (10300), 490 (6600), 568 nm ($2800 \text{ M}^{-1} \text{ cm}^{-1}$); $\lambda_{\text{max}}(\epsilon)$ for I^- : 360 (13000), 482 (6900), 710 nm ($1600 \text{ M}^{-1} \text{ cm}^{-1}$).

- 1 R. Cammack, M. Frey and R. Robson, *Hydrogen as a Fuel: Learning from Nature*, Taylor and Francis, London and New York, 2001.
- 2 A. Volbeda, M. H. Charon, C. Piras, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *Nature*, 1995, **373**, 580; Y. Higuchi, T. Yagi and N. Yasuoka, *Structure*, 1997, **5**, 1671; Y. Higuchi, H. Ogata, K. Miki, N. Yasuoka and T. Yagi, *Structure*, 1999, **7**, 549; M. Rousset, Y. Montet, B. Guigliarelli, N. Forget, M. Asso, P. Bertrand, J. C. Fontecilla-Camps and E. C. Hatchikian, *Proc. Natl. Acad. Sci. U. S. A.*, 1998, **95**, 11625; A. Volbeda, Y. Montet, X. Vernede, E. C. Hatchikian and J. C. Fontecilla-Camps, *Int. J. Hydrogen Res.*, 2002, **27**, 1449; P. M. Matias, C. M. Soares, L. M. Saraiva, R. Coelho, J. Morais, J. LeGall and M. A. Carrando, *J. Biol. Inorg. Chem.*, 2001, **6**, 63; E. Garcin, X. Vernede, E. C. Hatchikian, A. Volbeda, M. Frey and J. C. Fontecilla-Camps, *Structure*, 1999, **7**, 557.
- 3 F. A. Armstrong, *Curr. Opin. Chem. Biol.*, 2004, **8**, 133.
- 4 M. Stein and W. Lubitz, *J. Biol. Inorg. Chem.*, 2004, **98**, 862.

- 5 M. Stein and W. Lubitz, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5115; J. P. Whitehead, R. J. Gurbiel, C. Bagynka, B. M. Hoffmann and M. J. Maroney, *J. Am. Chem. Soc.*, 1993, **115**, 5629.
- 6 P. J. Silva, E. C. D. Van den Ban, H. Wassink, H. Haaker, B. de Castro, F. T. Robb and W. R. Hagen, *Eur. J. Biochem.*, 2000, **267**, 6541.
- 7 R. Mejia-Rodriguez, D. Chong, J. H. Reibenspies, M. P. Soriaga and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 2004, **126**, 12004; D. Chong, I. P. Georgakaki, R. Mejia-Rodriguez, J. Sanabria-Chinchilla, M. P. Soriaga and M. Y. Darensbourg, *Dalton Trans.*, 2003, 4158.
- 8 F. Gloaguen, J. D. Lawrence, T. B. Rauchfuss, M. Bénard and M. Rohmer, *Inorg. Chem.*, 2002, **41**, 6573.
- 9 A search in the Cambridge Structural Database (updated to May 2005) for $\text{Ni}(\mu\text{-S}_2)\text{Fe}$ resulted in 33 hits.
- 10 For discussion see: D. Sellmann, F. Lauderbach, F. Geipel, F. W. Heinemann and M. Moll, *Angew. Chem., Int. Ed.*, 2004, **43**, 3141.
- 11 L. Efros, H. H. Thorp, G. W. Brudvig and R. H. Crabtree, *Inorg. Chem.*, 1992, **31**, 1722.
- 12 G. Musie, J. H. Reibenspies and M. Y. Darensbourg, *Inorg. Chem.*, 1998, **37**, 302.
- 13 L. James, L. Cai, M. C. Muetteries and R. H. Holm, *Inorg. Chem.*, 1996, **35**, 4148.
- 14 Q. Wang, E. Barclay, A. J. Blake, E. S. Davies, D. J. Evans, A. C. Marr, E. J. L. McInnes, J. McMaster, C. Wilson and M. Schröder, *Chem.–Eur. J.*, 2004, **10**, 3384. See also: J. Lewis and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1982, 1085; D. J. E. Spencer, A. C. Marr and M. Schröder, *Coord. Chem. Rev.*, 2001, **219–221**, 1055; W. Zhu, A. C. Marr, Q. Wang, F. Neese, D. J. E. Spencer, A. J. Blake, P. A. Cooke, C. Wilson and M. Schröder, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 18280; P. A. Stenson, A. Marin-Becerra, C. Wilson, A. J. Blake, J. McMaster and M. Schröder, *Chem. Commun.*, 2006, 317.
- 15 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
- 16 S. Foerster, M. Stein, M. Brecht, H. Ogata, Y. Higuchi and W. Lubitz, *J. Am. Chem. Soc.*, 2003, **125**, 83; O. Trofanchuk, M. Stein, C. Gessner, F. Lenzian, Y. Higuchi and W. Lubitz, *J. Biol. Inorg. Chem.*, 2000, **5**, 36; M. Stein and W. Lubitz, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2668.