Synthesis, X-ray structure and electrochemical characterisation of a binuclear thiolate bridged Ni–Fe–nitrosyl complex, related to the active site of NiFe hydrogenase

Frank Osterloh,* Wolfgang Saak, Detlev Haase and Siegfried Pohl†

Fachbereich Chemie, Universität Oldenburg, Postfach 2503, D-26111 Oldenburg, Germany

[NiL] 1 (L = *N,N'*-diethyl-3,7-diazanonane-1,9-dithiolate) reacts with [Fe(CO)$_2$(NO)$_2$] 2 to afford [Ni(L)Fe(NO)$_2$] 3, in which a Ni^{II} ion and a nitrosylated Fe^{-II} centre are bridged *via* two μ-S atoms from the chelating ligand.

The NiFe hydrogenase from *D. gigas* catalyses the reversible oxidation of molecular hydrogen. This enzyme utilises a binuclear complex as the active site, in which one Ni and one Fe atom are covalently linked by the S atoms of two cysteine residues and by one unidentified ligand.[1–3] Two additional cysteine S atoms complete the square-pyramidal coordination sphere of Ni, whereas the Fe atom binds to three unidentified diatomic ligands, possible candidates being CO, CN$^-$, NO and C≡CH$^-$. These non-protein ligands give rise to unusual absorption bands (1800–2100 cm^{-1}) in the IR spectra of many NiFe hydrogenases and appear to be a constant feature of these enzymes.[1,4] These observations prompted us to search for synthetic pathways to binuclear, μ-S thiolate bridged NiFe complexes in which NO binds to an Fe atom.

When a solution of the neutral complex [NiL] 1 in acetonitrile is combined with a stoichiometric amount of liquid [Fe-(CO)$_2$(NO)$_2$] 2, the colour changes immediately from purple to deep brown. CO is liberated from the solution, indicating rapid substitution of CO by the Ni complex, a reaction type that has been well established on 2 with other nucleophiles.[5] The mixture was refluxed for 15 min to complete the reaction and then kept at room temperature for 24 h (Scheme 1).

Black needles of [Ni(L)Fe(NO)$_2$] 3 formed, which were filtered off, washed with acetonitrile and dried *in vacuo*. When the volume of the mother-liquor was reduced *in vacuo*, a second crop of 3 could be obtained, which had to be recrystallized from hot acetonitrile; the total yield was 57%.‡

The result of an X-ray structure analysis§ of 3 is shown in Fig. 1 and bond lengths and angles are given in Table 1. The most striking structural feature is the short Ni–Fe distance of 279.7(1) pm, which remains lower than the value of 290 pm of the binuclear complex of the active centre of NiFe hydrogenase.[1] Other known μ-SR bridged NiFe compounds exhibit Ni–Fe distances between 280.6(5) and 376(1) pm.[6–8] The small Ni–Fe separation in 3 is, at least in part, due to the low coordination number of the nitrosylated iron atom which is in a distorted tetrahedral N$_2$S$_2$ environment. The two NO ligands are slightly bent towards each other resulting in Fe–N–O angles of 167.0(5) and 174.6(5)°. These values are unexceptional; similar Fe–N–O angles were found in other complexes with S$_2$Fe(NO)$_2$ fragments, *e.g.* [(PhS)$_2$Fe(NO)$_2$]$^-$ [168.5(2), 169.4(2)°].[9] As in the latter complex, the NO groups in 3 are linear and hence must

be viewed as three-electron donors to the Fe atom, which is formally at the -ii oxidation level and has 18 valence electrons. Judged from structural details no significant electron delocalization from the reduced Fe centre to Ni^{II} takes place. Such a transfer of charge should influence the geometry of the Ni coordination environment, which apart from a decreased S–Ni–S angle (by 4°) and an increased N–Ni–N angle (by 3.7°) is almost identical to that of a similar mononuclear nickel(ii) complex.[10]

The IR spectrum of 3 shows two intense absorption bands at 1663 and 1624 cm^{-1}, which were assigned to the symmetrical and the asymmetrical stretching vibration of the nitrosyl ligands. The lowering of these values in comparison to 2 (1810 and 1766 cm^{-1} in cyclohexane)[11] indicates an increased transfer of electron density from Fe into π* orbitals of the NO ligands (back bonding), which is accompanied by a weakening of the NO triple bonds.

Although the IR spectrum of 3 does not reproduce the characteristic absorption pattern of NiFe hydrogenases at 1800–2100 cm^{-1}, a nitrosyl ligand at the active centre of NiFe hydrogenase cannot be excluded on the basis of IR spectroscopy. Variations of the band positions could result from
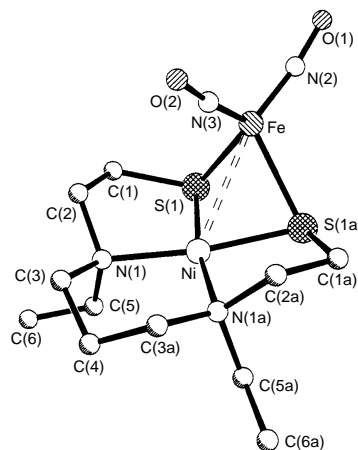

Fig. 1 Molecular structure of 3 with atom labelling scheme; 3 exhibits crystallographic mirror symmetry; H atoms have been omitted

Table 1 Selected interatomic distances (pm) and angles (°) for 3

Ni⋯Fe	279.7(1)	S(1)–Ni–S(1a)	81.46(6)
Ni–S(1)	217.6(1)	S(1)–Ni–N(1)	88.7(1)
Ni–N(1)	198.5(3)	N(1)–Ni–N(1a)	101.0(2)
Fe–S(1)	235.6(1)	S(1)–Fe–S(1a)	74.10(6)
Fe–N(2)	165.8(5)	S(1)–Fe–N(2)	113.6(2)
Fe–N(3)	164.7(6)	S(1)–Fe–N(3)	114.8(2)
N(2)–O(1)	118.3(7)	N(2)–Fe–N(3)	118.2(3)
N(3)–O(2)	119.7(7)	Ni–S(1)–Fe	76.11(4)
		Fe–N(2)–O(1)	167.0(5)
		Fe–N(3)–O(2)	174.6(5)
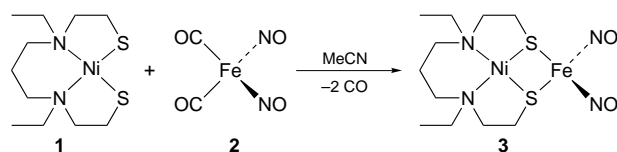
Scheme 1

different oxidation levels and from the different coordination environments of the Fe centres in both heterobimetallic complexes. However, it should be noted that other μ-SR bridged NiFe complexes, in which CO acts as a ligand to the Fe atom, mimic the IR properties of NiFe hydrogenases well.[8a]

In acetonitrile and dichloromethane solutions **3** can be quasi-reversibly oxidised at -120 mV (*vs.* SCE). Since the oxidation of N_2S_2 bound Ni^{II}, *e.g.* in $[Ni^{II}(NiL)_2]^{2+}$, cannot be achieved at potentials below $+860$ mV (*vs.* SCE in MeCN),[12] this process was tentatively assigned to the redox couple $Fe^{-II/-I}$. Interestingly, **2** in dmf solution can be consecutively reduced to the $[Fe(CO)_2(NO)_2]^{2-}$ dianion but has no tendency toward oxidation.[13] The differences in the redox properties of **2** and **3** have to be attributed to the better electron-donating capability of the μ-S thiolates in comparison to CO.

Attempts to oxidise **3** chemically have been unsuccessful. When treated with $[Fe(C_5H_5)_2]BF_4$ in dichloromethane or acetonitrile solution, **3** decomposes into various products, of which $[Ni^{II}(NiL)_2][BF_4]_2$ could be isolated as black or reddish needles, depending on the solvent. The formation of trinuclear cations, such as $[Ni^{II}(NiL)_2]^{2+}$ in which a central Ni^{II} binds to four bridging thiolate S atoms of two [NiL] fragments, has been commonly observed when Ni^{II} complexes like **1** are reacted with oxidising agents.[14]

We thank Dr H. Strasdeit for a critical review of the manuscript. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Footnotes

‡ The nickel complex **1** can be obtained as purple crystals by reaction of nickel(ii) acetylacetonate with H_2L in thf solution. H_2L is readily available by reaction of *N,N'*-diethyl-1,3-diaminopropane (Aldrich) with 2 equiv. of ethylenesulfide in toluene solution according to Karlin and Lippard.[15] **2** was synthesised from $Fe(CO)_5$ and $NaNO_2$–HOAc according to Hieber and Beutner.[16] *Analytical data* for **3**: IR (KBr): ν(NO) 1663vs, 1624vs cm^{-1}. UV–VIS spectrum (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) = 570 (370), 410 (1620). Satisfactory elemental analysis. Electrochemistry of **3** (in MeCN with $NBu^n_4PF_6$ as electrolyte): $E_0 = -120$ mV (*vs.* SCE); $\Delta E_p = 67$ mV; $i_c/i_a = 0.91$; scan rate 100 mV s^{-1}. **3** is readily soluble in dmf, MeCN and CH_2Cl_2. Crystals isolated from the reaction mixture were sufficient for X-ray crystallography.

§ *Crystal data* for **3**: $C_{11}H_{24}FeN_4NiO_2S_2$, $M = 423.02$, orthorhombic, space group *Pnma*, $a = 1177.0(1)$, $b = 1018.4(1)$, $c = 1471.2(1)$ pm, $U = 1.7635(3)$ nm^3, $T = 296$ K, $Z = 4$, $D_c = 1.593$ Mg m^{-3}, μ(Mo-Kα) = 2.134 mm^{-1}. A black single crystal of **3** with dimensions 0.72 $\times$ 0.40 $\times$ 0.28 mm was sealed in a glass capillary and mounted on a Siemens-Stoe AED 2 four-circle diffractometer. Data collection using Mo-Kα radiation ($\lambda = 71.073$ pm) and ω–2θ scans gave 1641 independent reflections ($\theta_{max} = 25°$), of which 1536 with $I > 2\sigma(I)$ were used in the final structure refinement. A semiempirical absorption correction using ψ-scans was applied. The structure was solved by direct methods and the solution developed using full-matrix least-squares refinements on F^2 and difference Fourier syntheses. Anisotropic displacement parameters were refined for all non-H atoms. H atoms were included on calculated positions with isotropic displacement parameters tied to those of the corresponding carbon atoms.[17] At convergence, $R_1 = 0.0497$, $wR_2 = 0.1099$, GOF = 1.295 for 106 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/446.

References

1 A. Volbeda, E. Garcin, C. Piras, A. L. de Lacey, V. M. Fernandez, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *J. Am. Chem. Soc.*, 1996, **118**, 12989.

2 A. Volbeda, M.-H. Charon, C. Piras, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *Nature*, 1995, **373**, 580; A. Volbeda, M.-H. Charon, C. Piras, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *J. Inorg. Biochem.*, 1995, **59**, 637.

3 M. A. Halcrow, *Angew. Chem.*, 1995, **107**, 1307; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1193.

4 T. M. Van Der Spek, A. F. Arendsen, R. P. Happe, S. Yun, K. A. Bagley, D. J. Stufkens, W. R. Hagen and S. P. J. Albracht, *Eur. J. Biochem.*, 1996, **237**, 629.

5 J. P. Crow, W. R. Cullen, F. G. Herring, J. R. Sams and R. L. Tapping, *Inorg. Chem.*, 1971, **10**, 1616; W. Hieber and J. S. Anderson, *Z. Anorg. Allg. Chem.*, 1933, **211**, 132.

6 F. Osterloh, W. Saak, D. Haase and S. Pohl, *Chem. Commun.*, 1996, 777; F. Osterloh and S. Pohl, unpublished work.

7 G. J. Colpas, R. O. Day and M. J. Maroney, *Inorg. Chem.*, 1992, **31**, 5053.

8 (*a*) C.-H. Lai, J. H. Reibenspies and M. Y. Darensbourg, *Angew. Chem.*, 1996, **108**, 2551; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2390; (*b*) D. K. Mills, Y. M. Hsiao, P. J. Farmer, E. V. Atnip, J. H. Reibenspies and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1991, **113**, 1421.

9 H. Strasdeit, B. Krebs and G. Henkel, *Z. Naturforsch. B*, 1986, **41**, 1357 and references therein.

10 G. J. Colpas, M. Kumar, R. O. Day and M. J. Maloney, *Inorg. Chem.*, 1990, **29**, 4779.

11 C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, 1960, 4842.

12 G. Musie, P. J. Farmer, T. Tuntulani, J. H. Reibenspies and M. Y. Darensbourg, *Inorg. Chem.*, 1996, **35**, 2176.

13 G. Piazza and G. Paliani, *Z. Phys. Chem.*, 1970, **71**, 91.

14 P. J. Farmer, T. Solouki, D. K. Mills, T. Soma, D. H. Russell, J. H. Reibenspies and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1992, **114**, 4601.

15 K. D. Karlin and S. J. Lippard, *J. Am. Chem. Soc.*, 1976, **98**, 6951.

16 W. Hieber and H. Beutner, *Z. Anorg. Allg. Chem.*, 1963, **320**, 101.

17 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; G. M. Sheldrick, SHELXTL-PC and SHELXL-93, University of Göttingen.