Characterisation of a triply thiolate-bridged Ni–Fe amine–thiolate complex: insights into the electronic structure of the active site of [NiFe] hydrogenase†‡

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Received (in Basel, Switzerland) 7th October 1999, Accepted 5th January 2000

The synthesis and structural characterisation of a new Ni–Fe amine–thiolate complex are described; its chemical properties are related to the active site of [NiFe] hydrogenase.

The active site of the [NiFe] hydrogenase from *D. gigas* consists of a (cys-S)$_2$Ni(μ-cys-S)$_2$XFe(CO)(CN)$_2$ bimetallic complex[1–3] that can exist in various redox states. Spectroscopic studies[4] and recent X-ray crystal structures of biological [NiFe] hydrogenases in their reduced, active forms[5] are indicative of changes in the electron density of both active site metal ions. The differences in the electron density could be due to the absence of a third bridging ligand X (which is a putative O^{2-} or OH$^-$ ion in the oxidized, inactive form) or by the electron count of the Ni–Fe cluster. Despite the discovery of these active site features, the mechanism of biological hydrogen activation is still not well understood.[6] Model compounds are therefore being studied to understand the function of the more complex enzymes.[7] They also hold promise for cheap hydrogen catalysts, for example, in solar energy conversion.[3] Current studies focus on mono- and binuclear Fe thiolate complexes with Fe(CO) and Fe(CN) fragments[8] and Ni thiolate complexes.[9] However, only a few relevant NiFe complexes have been described.[10] We here describe the syntheses, X-ray structure and properties of a new heterobinuclear NiFe amine–thiolate complex which differs from previous examples by its reversible redox reactions.

The new complex [Ni^{II}Fe^{II}(L)]$^+$ (**1a**, Scheme 1) was obtained by reaction of [Ni^{II}(L)]$^-$ (prepared *in situ* from the nonadentate N$_6$S$_3$ ligand H$_3$L·6HCl,[11] NiCl$_2$·6H$_2$O, and NEt$_3$) with one equivalent of anhydrous FeCl$_2$ in methanol. It was isolated as the one-electron-oxidized form [Ni^{II}Fe^{III}(L)]$^{2+}$ in {[Ni^{II}Fe^{III}(L)]$_2$Cl}[BPh$_4$]$_3$ (**1b**) by exposing the reaction mixture to air and adding excess NaBPh$_4$.§

Crystallographic characterization of complex **1b**¶ confirmed the crystal structure to consist of a face-sharing bioctahedral NiFe complex, [Ni^{II}Fe^{III}(L)]$^{2+}$. The different metal–ligand bond lengths reflect the heterobinuclear nature of the C_3-symmetric complex (Fig. 1). It is assigned a N′$_3$Ni^{II}(μ-SR)$_3$Fe^{III}N$_3$ core structure‖ as the average M–N and M–S bond lengths of the N′$_3$NiS$_3$ site at 2.083(4) and 2.430(1) Å, respectively, match more closely with those of related Ni^{II}N$_3$S$_3$ complexes.[11] The short average M–N and M–S bond lengths of the other N$_3$MS$_3$ site at 2.047(4) and 2.291(1) Å confirm this assignment. These distances are too short for an octahedral Ni^{II}N$_3$S$_3$ complex, but are in excellent accord with those of low-spin Fe^{III} complexes in an octahedral N$_3$S$_3$ environment.[12–14] Preliminary results of ^{57}Fe Mössbauer spectroscopic investigations also support this oxidation state distribution (Fig. 2). At T = 298 K, **1b** gives rise to a single quadrupole doublet with δ = 0.26 mm s^{-1} and $|\Delta E_Q|$ = 1.47 mm s^{-1}, while at T = 77 K, δ = 0.32 mm s^{-1} and $|\Delta E_Q|$ = 1.83 mm s^{-1}. The temperature dependence of the quadrupole

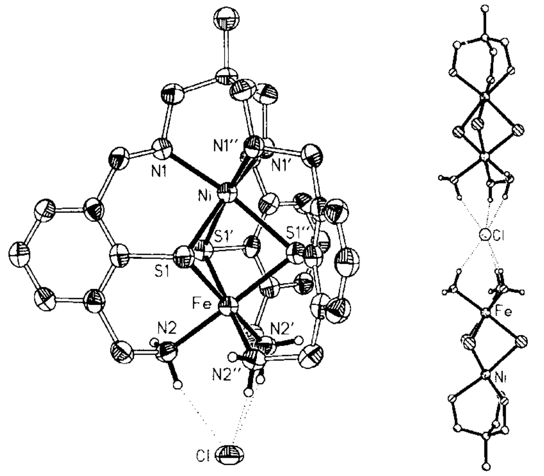
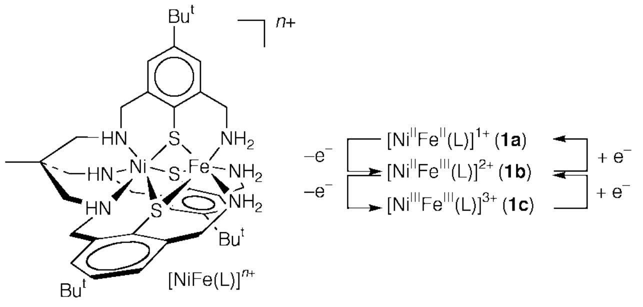


Fig. 1 Thermal ellipsoid plot of the [Ni^{II}Fe^{III}(L)]$^{2+}$ cation (left) and schematic representation of intermolecular hydrogen bonding interactions (right) in **1b**·12MeCN·H$_2$O. *tert*-Butyl groups and hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ni–N(1) 2.083(4), Ni–S(1) 2.430(1), Fe–N(2) 2.047(4), Fe–S(1) 2.291(1); Fe–S(1)–Ni 79.79(5). Symmetry codes used to generate equivalent atoms: 1 − *x*, *x* − *y*, *z* (′) and 1 − *x* + *y*, 1 − *x*, *z* (″).



Scheme 1

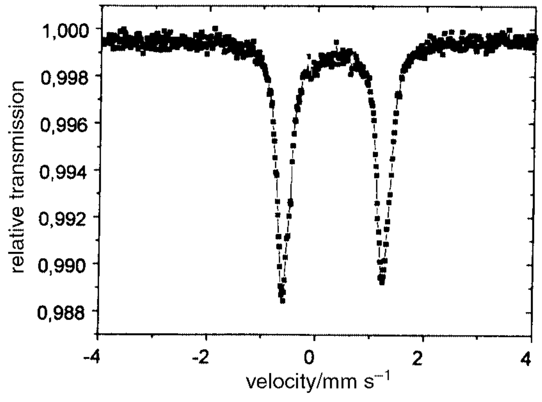


Fig. 2 ^{57}Fe Mössbauer spectrum of **1b**·12MeCN·H$_2$O at 77 K (relative to α-Fe).

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† Electronic Supplementary Information (ESI) available: CV; Electronic absorption, EPR and ^{57}Fe Mössbauer spectra. See http://www.rsc.org/suppdata/cc/a9/a908201h/

‡ Dedicated to Professor Dr H. Vahrenkamp on the occasion of his 60th birthday.

splitting is consistent with the presence of a low-spin Fe^{III} ion.

It should be noted that the Ni···Fe distance at 3.030(1) Å is slightly longer than the Ni···Fe separation of 2.90 Å reported for the as isolated, inactive form of [NiFe] hydrogenase. The wide M–S–M angles [79.79(5)°], however, imply little, if any, attraction between the metal atoms.[14] The intermolecular hydrogen bonding interactions found for **1b** in the solid state are also worth mentioning: a chloride ion links two $[NiFe(L)]^{2+}$ dications *via* six equivalent N–H···Cl hydrogen bonding interactions (N···Cl 3.208 Å). In the resulting LNiFe···Cl···FeNiL subunit the intermolecular Fe···Fe and Ni···Ni distances are at 7.910(1) Å and 13.971(1) Å, respectively. It is unclear at present whether this assembly is retained in solution.

The 77K EPR powder spectrum of **1b** displayed a complex multiplet centered at $g \approx 2$ as the main component, a weaker resonance was observed at $g \approx 4$ (see ESI). Room temperature magnetic susceptibility measurements revealed the complex to be a paramagnetic species with $\mu_{eff} = 2.3\ \mu_B$. The results are indicative of an $S = \frac{1}{2}$ spin ground state which is most likely attained by an intramolecular antiferromagnetic exchange interaction between the Ni^{II} ($S_1 = 1$) and low-spin Fe^{III} ($S_2 = \frac{1}{2}$) ions. A cyclic voltammogram of **1b** in DMF solution displays two electrochemically reversible one-electron steps at $E^1_{1/2}$ = +0.45 V [≡ $E_{1/2}(Ni^{III}Fe^{III}/Ni^{II}Fe^{III})$] and at $E^2_{1/2} = -0.43$ V [≡$E_{1/2}(Ni^{II}Fe^{III}/Ni^{II}Fe^{II})$] *vs.* SCE. The CV is significantly different from those of homobinuclear complexes, $[Ni_2(L)]^{n+}$ and $[Fe_2(L)]^{n+}$,[11] and unambiguously confirms the heterobinuclear nature of **1b**.

There is a clearly discernible mutual influence of the constituent Fe^{III} and Ni^{II} ions on the respective $M^{III/II}$ potentials. Comparison with the electrochemical properties of homodinuclear complexes $[Ni_2(L)]^{n+}$ and $[Fe_2(L)]^{n+}$ reveals that the ferric ion raises the $Ni^{III/II}$ couple by *ca.* +400 mV to more anodic potentials, whereas the divalent Ni ion shifts the $Fe^{III/II}$ potential to more cathodic potentials. It is therefore plausible to assume that the reverse effects would occur in a complex in which $E_{1/2}(Fe^{III/II}) > E_{1/2}(Ni^{III/II})$, as for instance in the hydrogenase active site. Since the strong field ligands CO and CN^- keep the iron atom formally at the +II oxidation level, a relatively low $Ni^{III/II}$ redox potential would result (at least for the oxidised, inactive form of the enzyme).

Compound **1b** is not a particularly close structural model of the active site of [NiFe] hydrogenase (lack of Fe-bound CO and CN^- ligands), however, it is an initial example for a thiolate-bridged NiFe complex which can exist in several different oxidation states. The effects of partial replacement of N or S donors of H_3L on the $M^{III/II}$ potentials of heterobinuclear NiFe complexes will be investigated in the future.

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. The authors thank Professor Dr C. Janiak for providing facilities for Mössbauer spectroscopic measurements.

Notes and references

§ An argon-purged solution of $H_3L·6HCl$ (96 mg, 0.10 mmol) and $NiCl_2·6H_2O$ (24 mg, 0.10 mmol) in methanol (10 mL) was treated with NEt_3 (90 mg, 0.90 mmol) to give a pale green solution. $FeCl_2$ (12.6 mg, 0.10 mmol) was then added. The mixture was stirred for 1 h under argon and then for 2 h with exposure to air. The resulting green-black solution was filtered. To the filtrate was added a solution of $NaBPh_4$ (0.17 g, 0.50 mmol) in methanol (1 mL). The green-black precipitate was isolated by filtration, washed with methanol and air-dried. Recrystallisation from acetonitrile afforded large single crystals of **1b**·12MeCN·H_2O (78 mg, 58%). CHN analyses for $\{[NiFe(L)]_2Cl\}[BPh_4]_3$ **1b**: found: C 68.23, H 6.57, N 5.97; calc. for $C_{154}H_{186}N_{12}S_6Ni_2Fe_2ClB_3$: C 68.65, H 6.96, N 6.24%.

¶ Crystal data for **1b**·12MeCN·H_2O: $C_{178}H_{224}N_{24}B_3ClFe_2Ni_2S_6O$, M_r = 3205.21, hexagonal, space group $R\bar{3}c$ (no. 167), T = 180(2) K, μ(Mo-Kα) = 0.51 mm^{-1}, a = 19.849(3) Å, c = 79.08(2) Å, V = 26982(8) Å^3, Z = 6; 54984 measured reflections, 7430 were unique [R(int) = 0.1943], structure determined by direct methods in SHELXS 86,[15] refinement with SHELXL-93,[15] R_1, wR_2 = 0.0687, 0.1675 [$I > 2\sigma(I)$]. CCDC 182/1512. See http://www.rsc.org/suppdata/cc/a9/a908201h/for crystallographic files in .cif format.

‖ N and N′ denote primary and secondary amine nitrogen atoms, respectively.

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Communication a908201h