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A Nickel(II)–Sulfur-Based Radical-Ligand Complex as a Functional Model of Hydrogenase

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Hydrogenases catalyze important biological hydrogen activation reaction [Eq. (1)].[1] Several models have been reported since the reports of the structure of hydrogenases from bacteria such as *Desulfovibrio gigas* and *Clostridium pasteurianum*.[2] Designing a nickel complex that can catalyze the reaction shown in Equation (1), in conjunction with the known electron paramagnetic resonance (EPR) active states, namely, Ni-A (unready), Ni-B (ready), Ni-C (active), Ni-L (light induced) and EPR inactive states, namely, Ni-SI (silent intermediate) and Ni-R (reduced), and is similar to native Ni-containing hydrogenases has not yet been achieved.[3]

$$2H^+ + 2e^- \leftrightarrow H_2 \qquad (1)$$

Electrochemical proton reduction by hydrogenase mimics is one of the current methods of estimating hydrogenase activity, which is correlated to the extent of the shift in proton reduction potentials under a catalyst towards zero volts (−0.42 V at pH 7.0). The complexes $[Fe_2(SR)_2(CN)_2(CO)_4]^{2-}$ and $[Fe_2(CN)(CO)_4H(PMe_3)(S_2C_3H_6)]^-$ reduce protons of organic acids to H_2 at a reduction potential of about −1 V.[4] An iron–sulfur cluster with a $Fe_{cubane}(\mu\text{-}SR)Fe_{subsite}$ linkage electrocatalytically assists proton reduction at $E_p = -1.13$ V.[5] Most of such functional catalysts are iron based and operate under higher reduction potentials. The interaction of protons with a nickel diphosphine complex, $[Ni(P_2^{Ph}N^{2Ph})_2(CH_3CN)][BF_4]_2$, has been investigated electrochemically and the proton reduction potential E_p^{red} is found to be shifted positively upon incorporation of this Ni complex onto carbon nanotubes (CNTs).[6] These nickel-based catalysts lack the sulfur donor atom present in native active sites. We present, herein, a complex with a $\{NiS_4\}$ core in the nickel(II) radical-ligand complex $[Ni^{II}(L^{2-})(L^{\cdot-})][PPh_4]$ (**1**; L = *cis*-1,2-dicarbomethoxyethylene dithiolate) displaying facile catalysis of the reaction shown in Equation (1). Complex **1** shows similar EPR spectra and redox potential values as those observed in native nickel hydrogenase. We report herein the electrochemical proton reduction efficiency of **1** in organic and aqueous acidic media at considerably lower reduction potentials.

Complex **1** has been prepared by an earlier reported method[7] and has now been characterized as $[Ni^{II}(L^{2-})(L^{\cdot-})][PPh_4]$ (Figure 1) instead of $[Ni^{III}(L_2)][PPh_4]$ based on X-ray structural, cyclic voltammetric, EPR spectroscopic, and electronic spectroscopic results. The crystals of **1** contain two crystallographically independent nickel complex

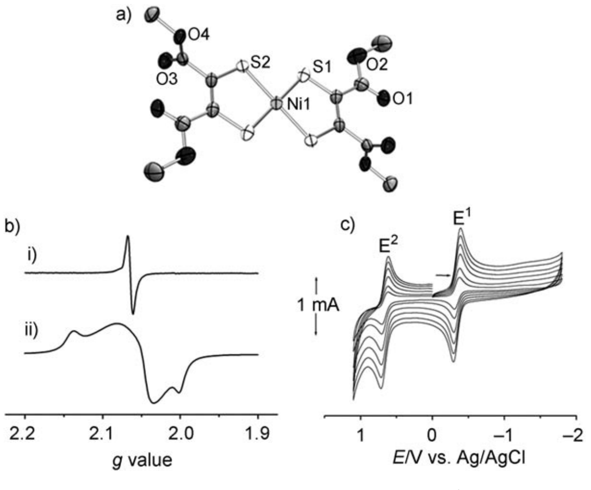

Figure 1. a) Perspective view of the monoanion $[Ni^{II}(L^{2-})(L^{\cdot-})]^-$, in crystals of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] are given in reference [9]. b) X-band EPR spectrum of **1** in DMF i) at 298 and ii) at 107 K. c) Cyclic voltammograms of **1** (2 mM) in CH_3CN/0.2 M tetrabutylammonium perchlorate (TBAP) at various scan rates (50–500 mV s^{-1}).

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anions of formula $[Ni^{II}(L^{2-})(L^{-\cdot})]^-$ and two PPh_4 cations in the lattice. The two anions are chemically identical although the geometric parameters of both are marginally different and the structure of one of the complex anion is shown in Figure 1 a.

In the complex anions of **1** the C–S bonds are shortened to an average of 1.728(5) and 1.719(9) Å, respectively, which is an indication of ligand oxidation to a radical. The average C–S bond length in the nickel(II) complex containing the pure dianionic form of this ligand, $[Ni^{II}(L_2)][PPh_4]_2$ is 1.744(2) Å.[7b] The reformulation of a dithiolene ligand, as shown above, with a radical character is now well established.[8] The reversible redox wave at $E^1_{1/2} = -0.341$ V versus Ag/AgCl observed in **1** (Figure 1 c) is similar to that of native Ni hydrogenase *Desulfovibrio gigas* (*D. gigas*) at −0.345 V versus Ag/AgCl (−0.390 V vs. SCE) at pH 7.[10] A quasi-reversible redox couple at $E^2_{1/2} = +0.664$ V versus Ag/AgCl is also observed for **1**, as shown in Figure 1 c. The EPR of **1** with *g* values of $g_1 = 2.13$, $g_2 = 2.04$, and $g_3 = 2.00$ are similar to the EPR active Ni-C state observed in Ni-containing hydrogenase of the species *D. gigas* (rhombic *g* values: 2.19, 2.16, 2.01) that is active towards hydrogen and the oxidation state of which has been debated to be Ni^I or Ni^{III}.[3] The radical character of **1** ($\mu_{eff} = 1.74\ \mu_B$) as envisaged from the electrochemical reduction potential $E^1_{1/2} = -0.341$ V, the intense intervalence charge-transfer band (IVCT) at 843 nm, $\varepsilon = 12300\ M^{-1}cm^{-1}$, and also from the similar EPR spectra to that of the electrochemically generated[9] $[Pd(L^{Bu\cdot})(bpy)]^+$ (L^{Bu} = 3,5-di-*tert*-butylbenzene-1,2-dithiolate, bpy = 2,2′-bipyridine) and the structurally characterized $[Ni^{II}(L^{Bu})(L^{Bu\cdot})]^-$ has been corroborated by DFT calculations (see below). DFT calculations using the X-ray structural parameters of the anions of **1** indicate that the SOMO is dominated by contributions from sulfur-based p orbitals with less d-orbital contributions, as shown in Figure 2 for one of the complex anions. The sum of spin density (Mulliken) on the four sulfur-based orbitals was found to be 60 %. Such radical-based metal–dithiolate system was suggested by the groups of Gray and Sawyer and has been extended recently by the groups of Wieghardt and Solomon,[8,11] Since the $E^1_{1/2}$ value of **1** is close to that observed in nickel-containing hydrogenase and the L-cysteine free radical showed similar anisotropic EPR *g* values (2.003, 2.025, and 2.053)[12] to those of **1**, the nature of the Ni-C state in the native hydrogenase of *D. gigas* may be radical based. This is important because the Ni-C state represents the key intermediate in the catalytic cycle. Based on this study the Ni-C state may be reinterpreted by considering ligand-based oxidations.[3,13]

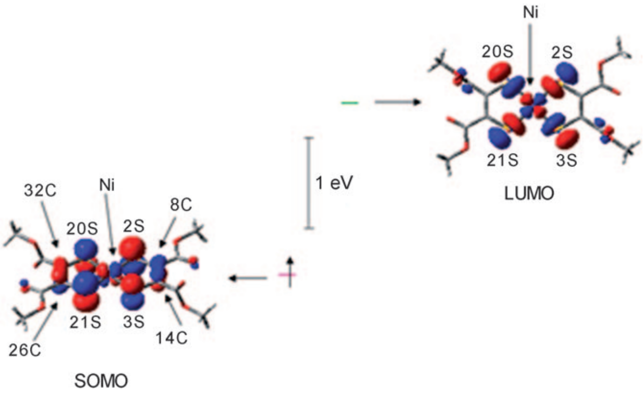

Figure 2. Visualization of Kohn–Sham molecular orbitals (MOs; SOMO and LUMO) and energy scheme of the complex anion $[Ni^{II}(L^{2-})(L^{-\cdot})]^-$, from spin-restricted ROB3LYP-DFT calculations. Percentage contributions of the selected orbitals: SOMO [%]: Ni(d) 21.24, 2S(p) 17.12, 3S(p) 11.38, 20S(p) 17.07, 21S(p) 11.39, 8C(p) 3.18, 14C(p) 2.49, 26C(p) 3.42, 32C(p) 2.49; LUMO [%]: Ni(d) 43.67, 2S(p) 15.29, 3S(p) 15.66, 20S(p) 15.62, 21S(p) 15.66. The energy difference, Δ*E*, between the SOMO and LUMO is 1.894 eV.

Complex **1** catalyzes the electrochemical proton reduction and the cyclic voltammetric results for the reduction of protons by using *p*-toluene sulfonic acid (TsOH) as a proton source are displayed in Figure 3 a. Two reduction peaks were observed, one corresponding to the ligand-based reduction originally observed in **1** and a new peak at $E^{red}_p = -0.69$ V versus Ag/AgCl, which is assigned to proton reduction. The current at $E^{red}_p = -0.69$ V increases accompanied by a negative shift to $E^{red}_p = -0.77$ V with increasing concentrations of added TsOH (Figure 3 a), which indicates the catalytic nature of the proton reduction. Complex **1** is the first example in Ni systems that electrocatalyzes proton reduction at such a low negative potential of −0.69 V versus Ag/AgCl on a GCE. TsOH undergoes reduction at $E^{red}_p = -1.71$ V in the absence of **1** under identical experimental conditions (see the Supporting Information).

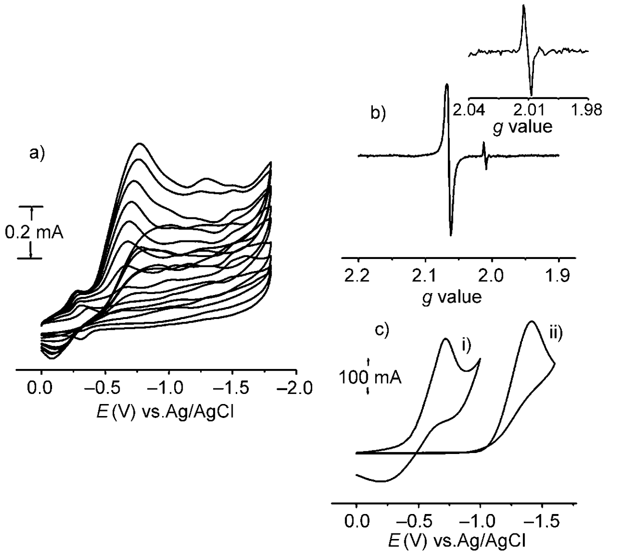

Figure 3. a) Cyclic voltammetric responses of **1** as a function of added TsOH of increasing concentrations (0.0017 g per addition) in CH_3CN (glassy carbon working electrode (GCE), TBAP, 0.2 M). b) EPR spectrum of **1** (2 mM/DMF) after the addition of TsOH at 298 K; inset: enlargement of the new signal that was observed after the addition of TsOH. c) Cyclic voltammograms of the reduction of TsOH in water ($NaClO_4$, 0.2 M); i) GCE surface coated with **1** (1 mM), ii) a polished GCE.

The electrochemical proton reduction of TsOH with the dianionic complex, $[Ni(mnt)_2][PPh_4]_2$[14] (mnt = maleonitriledithiolate) occurred at a higher reduction potential, $E_p^{red} = -1.25$ V (see the Supporting Information). Electrocatalysis by **1** at a much lower potential may be related to its unique radical nature, which should play an important role in lowering the reduction potential and in electron transfer to the bound protons. The iron complex $[Fe_2(CN)(CO)_4H(PMe_3)(S_2C_3H_6)]^-$ electrocatalyzes proton reduction at a higher reduction potential (−0.98 V), which is the lowest proton reduction potential known so far.[4a] Controlled potential electrolysis of a mixture of **1** (1 mmol) and TsOH (50 mmol) at −1.00 V in CH_3CN yielded a net charge of 52 mC over a period of 2 min, which was accompanied by the formation of gas bubbles on the GCE surface. The gas evolved was confirmed as hydrogen gas by gas chromatography (see the Supporting Information). Complex **1** also electrocatalyzes proton reduction in acidic aqueous medium using TsOH. In a typical experiment, a modified GCE was used, which was made by coating the polished GCE surface by dropping a solution of **1** (1 mmol) in CH_3CN and the GCE surface was dried with a blower for 10 min. The electrocatalytic proton reduction using this modified GCE in water medium containing TsOH showed a single reduction process at $E_p^{red} = -0.71$ V versus Ag/AgCl in water attributable to reduction of TsOH protons (Figure 3c). The reduction of TsOH in water using polished, unmodified GCE occurred at a very high negative potential of $E_p^{red} = -1.4$ V versus Ag/AgCl.

EPR and UV/Vis spectroscopy and ESI-MS studies suggest that the sulfur donor sites of **1** are protonated upon the addition of TsOH. Upon the addition of TsOH of varying concentrations, the intensity of the electronic absorption band at $\lambda_m = 453$ nm is decreased and the high intensity band at $\lambda_m = 843$ nm was found to decrease marginally (see the Supporting Information). The EPR spectrum of **1** in DMF at RT displayed a single line at $g = 2.06$ (cf. Figure 1b) and on addition of TsOH, a new signal at $g = 2.01$ appeared along with the original signal at $g = 2.06$ (Figure 3b and inset). The intensity of the EPR signal at $g = 2.01$ increased with the increasing concentrations of added TsOH. The negative ion ESI-MS spectral measurement of **1** with TsOH in CH_3CN showed the appearance of a peak at m/z 470.8, which could be assigned to $\{Ni^{II}(L_2)H\}$. The ^1H NMR spectrum of the mixture of **1** and TsOH in CD_3CN under argon did not show any signal in the negative region, which shows that a Ni hydride complex had not been formed. Curiously the spectrum displayed broadened signals due to the CH_3 ($\delta = 5.14$ ppm) and PPh_4 protons ($\delta = 7.45$, 7.62 and 7.88 ppm) along with a new weak signal at around $\delta = 4.1$ ppm, which is due to the protons attached to sulfur atoms of the dithiolene arising from protonation.[2g]

In summary, complex **1**, as a nickel(II)–sulfur-based radical-ligand complex, mimics the hydrogenase reaction. Complex **1** with the $\{NiS_4\}$ core electrocatalyzes hydrogen evolution at the lowest potential known so far of about $E_p = -0.69$ V in CH_3CN and in water at a reduction potential of $E_{p=} -0.71$ V versus Ag/AgCl. Spectral and electrochemical investigations of **1** in the presence of TsOH suggest that prior to proton reduction the sulfur donor site of the complex **1** is protonated.

Experimental Section

Synthetic procedure, spectral properties, x-ray structural data, and computational details of **1** are given in the Supporting Information. CCDC-770141 (**1**) contains 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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Keywords: cyclic voltammetry · density functional calculations · EPR spectroscopy · hydrogen evolution · hydrogenases

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[9] The EPR values, the short C1–S1 and C4–S2 bond lengths (1.734(5) and 1.722(5) Å, respectively), and a strong visible absorption (λ_{max} = 843 nm, ε = 12300 $\mathrm{M^{-1}cm^{-1}}$) suggest a radical character and that the unpaired electron is not centered on a purely metal-based orbital, for more details, see the main text.

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