

A Dithiolate-Bridged $(\text{CN})_2(\text{CO})\text{Fe}-\text{Ni}$ Complex Reproducing the IR Bands of $[\text{NiFe}]$ Hydrogenase

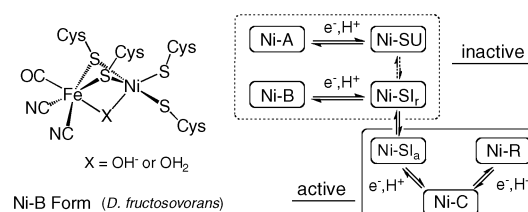
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A dithiolate-bridged dinuclear Fe–Ni complex, which has the desired *fac*-($\text{CN})_2(\text{CO})$ ligand set at iron, has been synthesized. Its CN/CO bands in the IR spectrum reproduce those of the Ni–A, Ni–B, and Ni–SU states, which indicate that these octahedral Fe^{II} centers have similar electronic properties. This result verifies the assignment of a $(\text{CN})_2(\text{CO})\text{Fe}^{\text{II}}$ moiety in the active site of $[\text{NiFe}]$ hydrogenase.

Chart 1



Hydrogenases are essential for hydrogen metabolisms of many microorganisms,¹ and the crystal structures of $[\text{NiFe}]$, $[\text{FeFe}]$, and $[\text{Fe}]$ hydrogenases have been determined.^{2–4} A unique feature of the $[\text{NiFe}]$ hydrogenase is that the Fe center carries CO and CN ligands,^{5,6} while the role of these ligands

in the enzymatic function is not yet well understood.⁷ On the basis of electron paramagnetic resonance, IR, and electrochemical measurements, various states of $[\text{NiFe}]$ hydrogenase have been identified as summarized in Chart 1, where the active site consists of a common $(\text{CN})_2(\text{CO})\text{Fe}$ moiety linked to a Ni atom by two cysteinyl thiolate bridges.

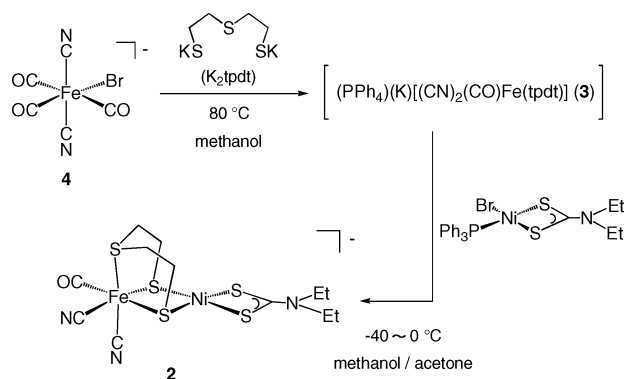
In the course of our studies of structural and functional models of the active sites of $[\text{NiFe}]$ hydrogenase,⁸ we have reported the syntheses of $(\text{PPh}_4)[(\text{CN})_2(\text{CO})_2\text{Fe}(\mu\text{-pdt})\text{Ni}(\text{S}_2\text{CNR}_2)]$ [**1**; pdt = 1,3-propanedithiolate, S_2CNR_2 = dithiocarbamates ($\text{R} = \text{Et}$, $\text{R}_2 = -(\text{CH}_2)_5-$)]^{8a} and a series of bis- and tris(thiolate)-bridged $\text{Fe}(\text{CO})_3\text{Ni}$ complexes.^{8c} Other dinuclear Fe–Ni model complexes previously reported, which have ligand sets such as aminethiolates, phosphines, $\eta^5\text{-C}_5\text{H}_5$, or nitric oxide, match the enzyme active sites less well compared with those in this report.⁹ Although the model complexes **1** are unique in that they possess the crucial CO/CN ligand set on iron, the number of CO ligands differs from that found in the enzyme active sites. This paper describes the synthesis of a thiolate-bridged $(\text{CN})_2(\text{CO})\text{Fe}-\text{Ni}$ complex, $[(\text{CN})_2(\text{CO})\text{Fe}(\mu\text{-tpdt})\text{Ni}(\text{S}_2\text{CNEt}_2)]^-$ (**2**;

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Scheme 1



tpdt = 3-thiapentanedithiolate¹⁰), from the reaction of preformed $[(\text{CN})_2(\text{CO})\text{Fe}(\text{tpdt})\text{K}]^-$ (**3**) and $(\text{PPh}_3)\text{NiBr}(\text{S}_2\text{CNEt}_2)$. With an $\text{Fe}(\text{CN})_2(\text{CO})$ fragment mimicking the enzyme active sites, complex **2** shows CN and CO bands closely resembling those of the Ni-A, Ni-B, and Ni-SU states of [NiFe] hydrogenase.

Two structurally characterized thiolate complexes of iron, $[(\text{CN})_2(\text{CO})\text{Fe}(\text{bdt})]^{2-}$ (bdt = 1,2-benzenedithiolate)¹¹ and $[(\text{CN})_2(\text{CO})\text{Fe}(\text{S}_3)]^{2-}$ [S_3 = bis(2-mercaptophenyl)sulfide],¹² have been reported that have the essential $(\text{CN})_2(\text{CO})\text{Fe}$ moiety. We have prepared $(\text{PPh}_4)[\text{Fe}(\text{CN})_2(\text{CO})_2(\text{pdt})\text{K}]$ from $(\text{PPh}_4)[(\text{CN})_2(\text{CO})_3\text{FeBr}]$ ($(\text{PPh}_4)[\textbf{4}]$)¹³ and $\text{K}_2(\text{pdt})$, for use as a building block for the synthesis of **1**.^{8a} Liaw et al. have reported the synthesis of the sulfur tridentate (tpdt^{2-}) complex, $[\text{N}(\text{PPh}_3)_2][(\text{CN})(\text{CO})_2\text{Fe}(\text{tpdt})]$, from the analogous reaction of $[\text{N}(\text{PPh}_3)_2][\textbf{4}]$ with $\text{Na}_2(\text{tpdt})$ in tetrahydrofuran at 40 °C.¹⁴ In contrast, when we carried out the reaction between $(\text{PPh}_4)[\textbf{4}]$ and $\text{K}_2(\text{tpdt})$ in methanol at 80 °C, the formation of **3** was detected by electrospray ionization mass spectrometry. The IR spectrum of the

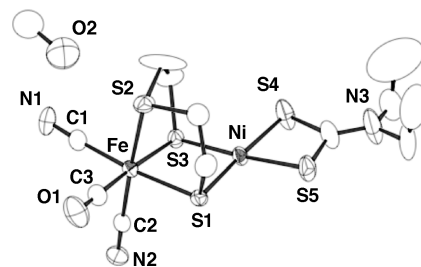


Figure 1. Structure of the complex anion of **2** with CH_3OH as a crystal solvent. The thermal ellipsoids are given at the 50% probability level. Selected bond distances (Å): Fe–Ni = 3.2960(5), Fe–C1 = 1.900(3), Fe–C2 = 1.904(2), Fe–C3 = 1.789(3), Fe–S1 = 2.2982(7), Fe–S2 = 2.2593(7), Fe–S3 = 2.3129(9), Ni–S1 = 2.2021(9), Ni–S3 = 2.1952(7).

reaction mixture exhibits a set of CN/CO bands, which indicates that **3** is the major product.¹⁵

We have successfully used **3**, generated in situ, as a synthon of the target dinuclear Fe–Ni complex **2**. Treatment of a methanol solution of **3** with an acetone solution of $(\text{PPh}_3)\text{NiBr}(\text{S}_2\text{CNEt}_2)$ at -40 °C resulted in a dark-brown solution, from which the dithiolate-bridged dinuclear complex **2** was isolated as a dark-brown powder in 51% yield based on $(\text{PPh}_4)[\textbf{4}]$. Single crystals of **2** were grown at 0 °C from an ether-layered methanol–acetonitrile solution, and X-ray analysis revealed that the desired $(\text{CN})_2(\text{CO})\text{Fe}$ moiety is retained during the formation of the Fe–Ni dinuclear structure. Complex **2** crystallized with one methanol molecule and one acetonitrile molecule each in the asymmetric unit as crystal solvents. Figure 1 shows the crystal structure of $\text{2} \cdot \text{CH}_3\text{OH} \cdot \text{CH}_3\text{CN}$, and selected bond distances are given in the caption. The Fe and Ni centers are bridged by the two thiolate S atoms of tpdt, and the $\text{Fe}(\mu\text{-S})_2\text{Ni}$ rhombus is slightly puckered along the S1–S3 vector with a dihedral angle of 14.7°. The Fe–Ni distance of 3.2960(5) Å is long, as are those of the oxidized forms of [NiFe] hydrogenase (2.8–2.9 Å). The Ni atom is further coordinated by the dithiocarbamate S atoms, conforming a square-planar geometry. With coordination of the thioether S atom of tpdt, the Fe center adopts an octahedral geometry. In the X-ray structure, the CN and CO ligands are distinguishable based on significantly different Fe–C bond lengths. The two long Fe–C bonds of 1.900(3) and 1.904(2) Å are assigned to CN ligands, while the short Fe–C bond of 1.789(3) Å is associated with CO, because CN is a weaker π acid. The two CN ligands are chemically inequivalent, being trans to a bridging thiolate sulfur or to a thioether S atom, although their Fe–C bond lengths are nearly identical. The asymmetric nature of **2** is corroborated by ^1H NMR, which exhibits eight sets of signals for the tpdt protons. The ^1H – ^1H NMR COSY spectrum further identified which sets of signals are coupled in the ^1H NMR spectrum. The coordination geometry at the Fe atom resembles that of $[(\text{CN})_2(\text{CO})\text{Fe}(\text{S}_3)]^{2-}$ [S_3 = bis(2-mercaptophenyl)sulfide].¹² Noteworthy here is the hydrogen bonding observed in the crystal between a CN ligand and the methanol molecule with a $\text{N} \cdots \text{O}$ distance of 2.923(6) Å. This hydrogen bond may be relevant to that

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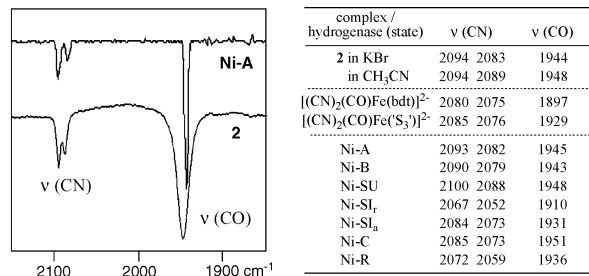


Figure 2. IR spectra of the Ni-A form of hydrogenase and **2**·CH₃OH·CH₃CN in KBr (left). At right, the CN/CO stretching frequencies (cm⁻¹) of **2**·CH₃OH·CH₃CN observed in KBr and CH₃CN are compared with those of various states of the [NiFe] hydrogenase from *A. vinosum*.^{5c}

found in the protein crystal structures of hydrogenases. For instance, the O(H) and N(H) atoms of Ser499 in the enzyme of *Desulfovibrio fructosovorans* are both located 2.9 Å away from a CN nitrogen of the active site, while the other CN ligand may also form a hydrogen bond with one of the two N(H) groups of Arg476 ($N_{\text{CN}} \cdots N_{\text{NH}} = 2.8$ Å).¹⁶

The IR spectrum of **2**·CH₃OH·CH₃CN in KBr is reproduced in the lower left part of Figure 2, where the two bands at 2094 and 2083 cm⁻¹ are assigned to C–N stretching modes (ν_{CN}) and an intense ν_{CO} band appears at 1944 cm⁻¹. The CN and CO bands are both shifted to lower frequencies compared with those of (PPh₄)[(CN)₂(CO)₂Fe(μ -pdt)Ni(S₂CNEt₂)] ($\nu_{\text{CN}} = 2108$ and 2092 cm⁻¹, $\nu_{\text{CO}} = 2031$ –2015 and 1975–1959 cm⁻¹) because the smaller number of CO ligands in **2** leads to greater π -back-donation from the Fe center. The CN–CH₃OH hydrogen bond found in the X-ray structure of **2**·CH₃OH·CH₃CN may also contribute to the ν_{CN} shift. Given the facial (CN)₂(CO) ligand arrangement on Fe in the dinuclear Fe–Ni structure, a sensible comparison between the CN/CO bands of **2** and [NiFe] hydrogenase, which are listed on the right side of Figure 2, can be made. In fact, the IR spectrum of **2** in the

1900–2150 cm⁻¹ region resembles closely that of the Ni–A state of *Allochromatium vinosum* hydrogenase.^{5c} The ν_{CN} and ν_{CO} values of the Ni–B and Ni–SU states are also similar, while those for the other hydrogenase states of *A. vinosum* are systematically lower. Notably, a CH₃CN solution of half-sandwich iron complex K[(η^5 -C₅H₅)Fe(CN)₂(CO)] also gives CO/CN bands that match those of the active site.¹⁷ On the other hand, for the mononuclear dithiolate complex anions containing the (CN)₂(CO)Fe moiety, [(CN)₂(CO)–Fe(bdt)]²⁻,¹¹ and [(CN)₂(CO)Fe(“S₃”)]²⁻,¹² their IR spectra in CH₃CN match less well those of the Ni–A, Ni–B, and Ni–SU states of the [NiFe] enzyme (Figure 2).

In summary, we have synthesized a dithiolate-bridged dinuclear Fe–Ni complex **2**, which has the desired *fac*-(CN)₂(CO) ligand set at iron. The square-planar Ni^{II} center of **2** differs from the Ni sites of Ni–A/Ni–B and Ni–SU states of [NiFe] hydrogenase, which are thought to contain pentacoordinated Ni^{III} and Ni^{II} centers.^{2,5,6} Nevertheless, the CN/CO bands in the IR spectrum of **2** reproduce those of the Ni–A, Ni–B, and Ni–SU states, which indicate that both of these octahedral Fe^{II} centers have similar electronic properties. This result verifies the assignment of a (CN)₂(CO)Fe^{II} moiety in the active site of [NiFe] hydrogenase.

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Supporting Information Available: Experimental details and spectral data and information on X-ray analysis and a CIF file of the X-ray crystallographic data for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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