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

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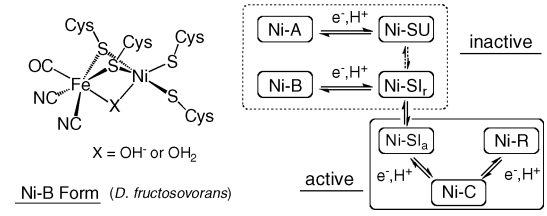
A dithiolate-bridged dinuclear Fe−Ni complex, which has the desired *fac*-$(CN)_2(CO)$ ligand set at iron, has been synthesized. Its CN/CO bands in the IR spectrum reproduce those of the Ni−A, Ni−B, and Ni−SU states, which indicate that these octahedral Fe^{II} centers have similar electronic properties.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

Hydrogenases are essential for hydrogen metabolisms of many microorganisms,[1] and the crystal structures of [NiFe], [FeFe], and [Fe] hydrogenases have been determined.[2−4] A unique feature of the [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 [NiFe] hydrogenase have been identified as summarized in Chart 1, where the active site consists of a common $(CN)_2(CO)Fe$ moiety linked to a Ni atom by two cysteinyl thiolate bridges.

Chart 1



In the course of our studies of structural and functional models of the active sites of [NiFe] hydrogenase,[8] we have reported the syntheses of $(PPh_4)[(CN)_2(CO)_2Fe(\mu\text{-pdt})Ni(S_2CNR_2)]$ [**1**; pdt = 1,3-propanedithiolate, S_2CNR_2 = dithiocarbamates (R = Et, $R_2 = -(CH_2)_5-$)][8a] and a series of bis- and tris(thiolate)-bridged $Fe(CO)_3Ni$ complexes.[8c] Other dinuclear Fe−Ni model complexes previously reported, which have ligand sets such as aminethiolates, phosphines, η^5-C_5H_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 $(CN)_2(CO)$-Fe−Ni complex, $[(CN)_2(CO)Fe(\mu\text{-tpdt})Ni(S_2CNEt_2)]^-$ (**2**;

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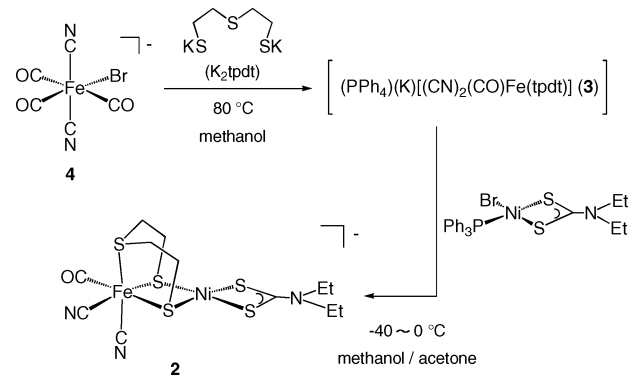
Scheme 1



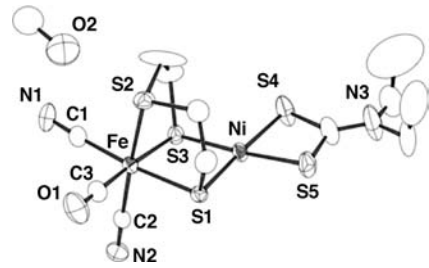


Figure 1. Structure of the complex anion of **2** with CH_3OH as a crystal solvent. The thermal ellipsoids are given at the 50% probability level. Selected bond distances (Å): Fe−Ni = 3.2960(5), Fe−C1 = 1.900(3), Fe−C2 = 1.904(2), Fe−C3 = 1.789(3), Fe−S1 = 2.2982(7), Fe−S2 = 2.2593(7), Fe−S3 = 2.3129(9),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

tpdt = 3-thiapentanedithiolate[10]), from the reaction of preformed $[(CN)_2(CO)Fe(tpdt)K]^-$ (**3**) and $(PPh_3)NiBr(S_2CNEt_2)$. With an $Fe(CN)_2(CO)$ 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, $[(CN)_2(CO)Fe(bdt)]^{2-}$ (bdt = 1,2-benzenedithiolate)[11] and $[(CN)_2(CO)Fe(\text{“}S_3\text{”})]^{2-}$ [“S_3” = bis(2-mercaptophenyl)sulfide],[12] have been reported that have the essential $(CN)_2(CO)Fe$ moiety. We have prepared $(PPh_4)[Fe(CN)_2(CO)_2(pdt)K]$ from $(PPh_4)[(CN)_2(CO)_3FeBr]$ ((PPh_4)[**4**])[13] and K_2(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, $[N(PPh_3)_2][(CN)(CO)_2Fe(tpdt)]$, from the analogous reaction of $[N(PPh_3)_2]$[**4**] with Na_2(tpdt) in tetrahydrofuran at 40 °C.[14] In contrast, when we carried out the reaction between (PPh_4)[**4**] and K_2(tpdt) in methanol at 80 °C, the formation of **3** was detected by electrospray ionization mass spectrometry. The IR spectrum of the 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 $(PPh_3)NiBr(S_2CNEt_2)$ 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 (PPh_4)[**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 $(CN)_2(CO)Fe$ 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 **2**·CH_3OH·CH_3CN, and selected bond distances are given in the caption. The Fe and Ni centers are bridged by the two thiolato S atoms of tpdt, and the $Fe(\mu\text{-}S)_2Ni$ 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 thiolato sulfur or to a thioether S atom, although their Fe−C bond lengths are nearly identical. The asymmetric nature of **2** is corroborated by ^{1}H NMR, which exhibits eight sets of signals for the tpdt protons. The ^{1}H−^{1}H NMR COSY spectrum further identified which sets of signals are coupled in the ^{1}H NMR spectrum. The coordination geometry at the Fe atom resembles that of $[(CN)_2(CO)Fe(\text{“}S_3\text{”})]^{2-}$ [“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 N···O distance of 2.923(6) Å. This hydrogen bond may be relevant to that

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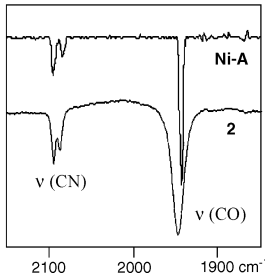

complex / hydrogenase (state)	ν (CN)		ν (CO)
2 in KBr	2094	2083	1944
in CH_3CN	2094	2089	1948
$[(CN)_2(CO)Fe(bdt)]^{2-}$	2080	2075	1897
$[(CN)_2(CO)Fe('S_3')]^{2-}$	2085	2076	1929
Ni-A	2093	2082	1945
Ni-B	2090	2079	1943
Ni-SU	2100	2088	1948
$Ni\text{-}SI_r$	2067	2052	1910
$Ni\text{-}SI_a$	2084	2073	1931
Ni-C	2085	2073	1951
Ni-R	2072	2059	1936

Figure 2. IR spectra of the Ni−A form of hydrogenase and **2**·CH_3OH·CH_3CN in KBr (left). At right, the CN/CO stretching frequencies (cm^{-1}) of **2**·CH_3OH·CH_3CN observed in KBr and CH_3CN 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 ($N_{CN}\cdots N_{NH} = 2.8$ Å).[16]

The IR spectrum of **2**·CH_3OH·CH_3CN 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 $(PPh_4)[(CN)_2(CO)_2Fe(\mu\text{-}pdt)Ni(S_2CNEt_2)]$ ($\nu_{CN} = 2108$ and 2092 cm^{-1}, $\nu_{CO} = 2031-2015$ 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 $CN-CH_3OH$ hydrogen bond found in the X-ray structure of **2**·CH_3OH·CH_3CN 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 CH_3CN solution of half-sandwich iron complex $K[(\eta^5\text{-}C_5H_5)Fe(CN)_2(CO)]$ 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, $[(CN)_2(CO)\text{-}Fe(bdt)]^{2-}$,[11] and $[(CN)_2(CO)Fe(\text{“}S_3\text{”})]^{2-}$,[12] their IR spectra in CH_3CN 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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