Carbon Monoxide and Cyanide Ligands in a Classical Organometallic Complex Model for Fe-Only Hydrogenase**

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As for the well-characterized [NiFe]hydrogenase,[1] IR spectroscopic studies[2] and X-ray crystal structures of Fe-only hydrogenases isolated from *Clostridium pasteurianum*[3] and *Desulfovibrio desulfuricans*[4] suggest the active site contains diatomic ligands, CN^- and CO. The stick drawing representation in Figure 1 embodies features of the diiron site

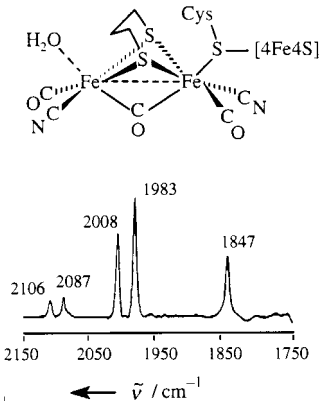

Figure 1. Top) Representation of the dinuclear iron site of Fe-only hydrogenases as an amalgamation of two reported structures, see text.[3, 4] Bottom) The IR spectrum in the diatomic region as recorded on the oxidized form of the hydrogenase isolated from *Desulfovibrio vulgaris*. (Spectrum reproduced from reference [2].

of both Fe-only H_2ase structures. For example, the former did not refine the S–S bridge as the hydrocarbon link $(CH_2)_3$,[3] while the latter did not assign the third bridging ligand as a CO group,[4] a conclusion which is consistent with IR spectra measured on yet a third Fe-only H_2ase source, *Desulfovibrio vulgaris* (Figure 1, bottom).[2] While the similarity of peptide sequence at the H-cluster in the different Fe-only H_2ases would support this melding of structures,[4] the changes in the ν(CO) and ν(CN) IR spectral region with various manipulations of the protein[2] could indicate the possibility of different forms of the active site dinuclear unit. The development of organometallic complexes as spectroscopic models is hence an important goal as vibrational spectroscopy is a powerful tool for defining electronic factors that control structure and reactivity in traditional organometallic chemistry.

The surprising and useful similarity between the classical organometallic complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(CN)_2]^-$ and the iron site of [NiFe]hydrogenase[5] appears to be equally matched by a homodinuclear organometallic mimic of the unique diiron center in the Fe-only H_2ases. The $[(\mu\text{-}SCH_2CH_2CH_2S)Fe_2(CO)_6]$[6] complex (hereafter, $[(\mu\text{-pdt})Fe_2(CO)_6]$) is a member of a well-known set of $[(\mu\text{-}SR)_2Fe_2(CO)_{6-x}L_x]$ complexes which are thermodynamic sinks in low-valent iron–thiolate carbonyl chemistry. Herein we report its molecular structure and studies of CO lability and reactivity resulting in the preparation of spectroscopically relevant mono- and dianionic cyano dimetallic complexes.

Orange platelike crystals of $[(\mu\text{-pdt})Fe_2(CO)_6]$ obtained from crystallization from pentane are in the space group $P2_1/m$.[7]

The molecular structure of the compound is displayed in Figure 2 (top). Distances and angles are essentially the same

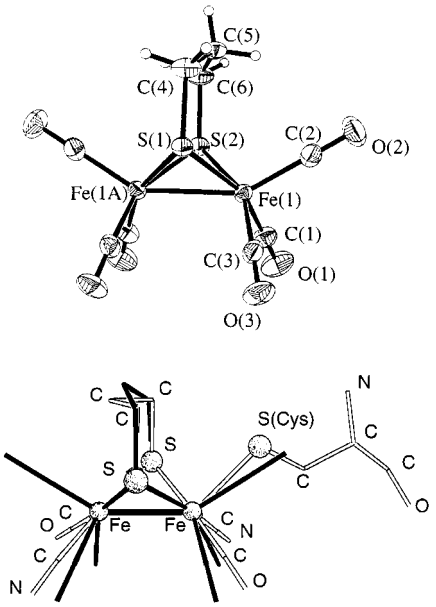

Figure 2. Top) Molecular structure of $[(\mu\text{-}SCH_2CH_2CH_2S)Fe_2(CO)_6]$ (ORTEP plot, thermal ellipsoids at 50% probability) Selected bond lengths [Å] and angles [°]: Fe(1)–Fe(1A) 2.5103(11), Fe(1)–S(1) 2.2542(10), Fe(1)–S(2) 2.2491(10), S(1)–C(4) 1.823(4), S(2)–C(6) 1.818(4), C(4)–C(5) 1.451(7), C(6)–C(5) 1.470(7), Fe(1)–C(1) 1.801(3), Fe(1)–C(2) 1.802(3), Fe(1)–C(3) 1.797(3), C(1)–O(1) 1.141(4), C(2)–O(2) 1.130(4), C(3)–O(3) 1.136(4); S(1)-Fe-S(2) 85.27(4), Fe(1)-S(1)-Fe(1A) 67.67(4), Fe(1)-S(2)-Fe(1A) 67.85(4), C(1)-Fe-C(2) 97.96(14), C(2)-Fe-C(3) 100.01(13), C(1)-Fe-C(3) 91.02(14), C(1)-Fe-S(1) 160.15(11), C(1)-Fe-S(2) 97.79(11), C(2)-Fe-S(1) 101.75(10), C(2)-Fe-S(2) 103.96(10), C(3)-Fe-S(2) 155.93(10). Bottom) Superposition of the structures of $[(\mu\text{-}SCH_2CH_2CH_2S)Fe_2(CO)_6]$ with the Fe–Fe dimetallic site of Fe-only hydrogenase using the crystal structure coordinates of the protein as isolated from *Desulfovibrio desulfuricans*.[4]

in the $[(\mu\text{-EtS})_2Fe_2(CO)_6]$-analogous structure as well as in the two-carbon linked, $[(\mu\text{-}SCH_2CH_2S)Fe_2(CO)_6]$ complex.[11, 12] The coordination geometry about each iron center is roughly square pyramidal; the two μ-S atoms, C(1), and C(3) define the base, and C(2), the apical position. The metal is displaced by about 0.38 Å from the base, resulting in the obtuse angles

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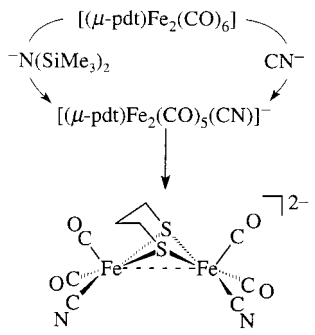
between the atoms at apical and basal sites. This edge-shared bi-square pyramidal interpretation differs from earlier structural reports of $[(\mu\text{-SR})_2Fe_2(CO)_6]$ which represented the $\{Fe(CO)_3\}$ fragment as part of a face-sharing bioctahedron, the sixth site of which was a shared vertex, the metal–metal bond. The Fe–Fe bond was frequently shown as bent, reflecting the directionality of the overlapping metal orbitals.[11, 13] While the short Fe–Fe distances of $[(\mu\text{-pdt})Fe_2(CO)_6]$ and those found in the enzyme structures (vide infra) are well within the accepted range for Fe–Fe bonds, and a metal–metal bond is expected to spin pair the 17-electron $\{(RS)_2Fe(CO)_3\}$ fragments accounting for the observed diamagnetism, the exact nature of the HOMO has not been defined.

Figure 2 (bottom) displays the model complex $[(\mu\text{-pdt})Fe_2(CO)_6]$ overlaid with the Fe–Fe dimetallic site in the hydrogenase isolated from *D. desulfuricans*.[4] The Fe–Fe distance of 2.510(1) Å in the model complex is 0.1 Å shorter than those reported for the diiron site in the protein structures (2.62 and 2.60 Å).[3,4] The root mean square (rms) deviation of the eight atoms, 4 Fe and 4 S, used to determine the fit, 0.0489 Å, is impressive as is the electron density match of the pdt-bridged diiron site, and the overall coordination of the irons. There is some misalignment in the pdt units, particularly at the central CH_2 group. The slight misfit could imply protein restriction, or, since the S–S linker could not be defined in the *C. pasteurianum* enzyme structure,[3] give cause to further examine the assignment of the remarkable unit. Interestingly, the limited covalent interactions with the protein has prompted the suggestion that the organodimetallic moiety might have been imported as a preconstructed unit.[4]

Dissolved in THF, the orange-red $[(\mu\text{-pdt})Fe_2(CO)_6]$ compound exchanged carbonyl ligands slowly with ^{13}CO even with photolysis. In contrast, addition of excess cyanide as Et_4NCN in solution in CH_3CN or as [15]crown-5-solubilized KCN in THF, resulted in red shifts in the diatomic ν(CO) region within a few hours, consistent with stepwise substitution of CO by two CN^- ions. An alternate route to the expected monocyano derivative $[(\mu\text{-pdt})Fe_2(CO)_5(CN)]^-$, that is the reaction of $[(\mu\text{-pdt})Fe_2(CO)_6]$ with sodium bis(trimethylsilyl)amide in THF, demonstrated a coincidence of spectral bands of the intermediate produced by ligand substitution (Scheme 1, Figure 3). A weak band which appeared at 2103 cm^{-1} was assigned to a single ν(CN) band, resulting from the nucleophilic addition of one $N(SiMe_3)_2^-$ ion with subsequent loss of the silyl ether (Scheme 1). The ν(CO) region was



Scheme 1. Ligand substitution in $[(\mu\text{-pdt})Fe_2(CO)_6]$.

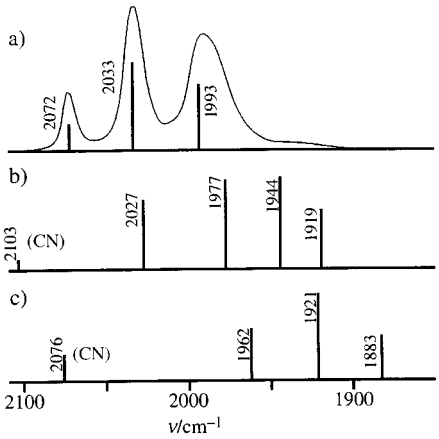


Figure 3. Line drawings of the IR spectra in the diatomic region of a) $[(\mu\text{-}SCH_2CH_2CH_2S)Fe_2(CO)_6]$, b) $[(\mu\text{-}SCH_2CH_2CH_2S)Fe_2(CO)_5(CN)]^-$, and c) $[(\mu\text{-}SCH_2CH_2CH_2S)Fe_2(CO)_4(CN)_2]^{2-}$.

rendered more complicated than that of the $[(\mu\text{-pdt})Fe_2(CO)_6]$ precursor, as expected for the loss of symmetry. Band shifts in the ν(CO) region as large as 75 cm^{-1} resulted from incorporation of a cyanide ligand, which produced a unit negative charge on one iron.[14]

While subsequent addition of $Na[N(SiMe_3)_2]$ produced no further reaction,[15, 16] a second CN^- was incorporated by the ligand exchange process. A medium to weak broad band appearing at 2076 cm^{-1}, unfortunately coincident with the highest frequency CO band of the neutral starting material, was established by isotopic labeling (using both $K^{13}CN$ and $KC^{15}N$) to be the ν(CN) band.[17]

The structural assignment of $[(\mu\text{-pdt})Fe_2(CO)_4(CN)_2]^{2-}$ is shown in Scheme 1. The line drawing spectrum of the final product (Figure 3c) indicates a relative intensity pattern compatible with a symmetrical placement of two, vibrationally uncoupled (or very weakly coupled), cyanide ligands on adjacent iron centers.[18] The displacement of vibrationally coupled major ν(CO) bands by 80–100 cm^{-1} to lower energy from the starting material furthermore suggests symmetrical disubstitution of two carbonyl ligands by cyanide ligands with a unit negative charge on each iron center.

A comparison of the spectra shown in Figure 1 and Figure 3 reveal that the model anionic, cyanoiron(I) species have ν(CO) bands somewhat lower in frequency than those of the aerobically isolated and presumably oxidized enzyme.[2] Initial IR studies of the reduced enzyme however find both ν(CO) and ν(CN) bands compatible with our anionic cyano Fe^I–Fe^I dinuclear models.[2] The actual oxidation state of the dinuclear iron site in the enzyme and whether, or how, it changes with various enzymic redox levels is not yet established.

Inorganic and organometallic precedents of CO coordination to iron in higher oxidation states are few and highlight the necessity of good donor ligands such as thiolates and cyanides to stabilize $Fe^{II}(CO)$ or $Fe^{III}(CO)$ as seen in the case of the mononuclear $[Fe^{II}(PS3)(CO)(CN)]^{2-}$ and $[Fe^{III}(PS3)(CO)(CN)]^-$ complexes ($PS3H_3$ = tris(2-sulfanylphenyl)phosphane) reported by Koch and co-workers.[19] Furthermore, the $[(\eta^5\text{-}C_5H_5)Fe^{II}(CO)(CN)_2]^-$ ion provided a precise match of ν(CO) and ν(CN) in the oxidized form of $[NiFe]H_2$ase, confirming

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the proposed oxidation state of Fe^{II} in the $[(SCys)_2Ni^{III}(\mu\text{-}SCys)_2Fe^{II}(CO)(CN)_2]$ site.[5] A highly asymmetric model complex which contains $\{Fe^{II}\text{-}(\mu\text{-}SR)_3\text{-}Fe^{II}(CO)_2\}$ shows ν(CO) bands at 2011 and 1957 cm^{-1}, considerably higher than the average ν(CO) band of the reduced Fe-only H_2ase enzyme.[20] Furthermore, its Fe···Fe distance of about 3.1 Å is typical of Fe^{II}-bridged thiolates.

The structural and spectroscopic matches of the Fe-only H_2ase and the model dinuclear complexes reported herein indicate the possibility of Fe^{I} in nature, or the achievement of an equivalent electron density about Fe^{II} by the use of anionic cyanide ligands. The ambidentate CN^- provides an anchor for the site through H-bonding to the protein, which in turn may tune the amount of negative charge contributed to the iron centers.[21] Notably, the other component of the "H-cluster", cysteine-S bridged into the dinuclear site, is a 4Fe4S cube which may serve as an oxidation level buffer. The 2Fe/4Fe4S site would appear to be electronically versatile and hence complicated, as noted in forerunner spectroscopic studies.[22]

Experimental Section

Synthesis of $[(\mu\text{-pdt})Fe_2(CO)_6]$: The $[(\mu\text{-pdt})Fe_2(CO)_6]$ complex was obtained either from $BrCH_2CH_2CH_2Br$ and $[(\mu\text{-}S_2)Fe_2(CO)_6]$,[6, 23] or from reaction of $HSCH_2CH_2CH_2SH$ with $Fe_3(CO)_{12}$.[24]

Reaction of $[(\mu\text{-pdt})Fe_2(CO)_6]$ with $Na[N(SiMe_3)_2]$: To a solution containing $[(\mu\text{-pdt})Fe_2(CO)_6]$ (ca. 0.16 g, 0.41 mmol) in dry THF (20 mL) was added a solution of $Na[N(SiMe_3)_2]$ (0.134 g, 0.732 mmol) in THF. The ensuing color change from dark orange to deep red brown was accompanied by IR spectral changes (see Figure 3).

Synthesis of $[(\mu\text{-pdt})Fe_2(CO)_4(CN)_2]^{2-}$ by ligand substitution: To $[(\mu\text{-pdt})Fe_2(CO)_6]$ (0.056 g, 0.15 mmol) dissolved in CH_3CN (15 mL) was added Et_4NCN (0.054 g, 0.35 mmol) in CH_3CN (5 mL) . Within 6 h the limiting IR spectrum, Figure 3c, was obtained.

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[7] Crystal data: for $C_9H_6O_6S_2Fe_2$, $M_r = 385.96$, monoclinic, space group $P2_1/m$, $a = 6.795(3)$, $b = 13.422(4)$, $c = 7.833(2)$ Å, $\beta = 108.06(2)^\circ$, $V = 679.2(4)$, $F(000) = 384$, $\rho = 1.887\ g\,cm^{-3}$, $Z = 2$, $\mu(Mo_{K\alpha}, \lambda = 0.71073) = 2.458\ mm^{-1}$. Intensity data were collected to a θ limit of 25.01° on a Siemens P4 single crystal diffractometer[8] at 197 K and corrected for absorption ($T_{min} = 0.5713$, $T_{max} = 0.9940$). The structure was solved by direct methods[9] and refined by full-matrix least-squares analysis of all data on F^2.[10] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model. Refinement of 97 parameters and 1208 data points converged with residual values of $R(F)$ (all data) = 0.0380, $R(F)[I > 2\sigma(I)] = 0.317$, $R_w(F^2)$ (all data) = 0.0881, $\Sigma(F^2)$ (all data) = 1.016. The propanedithiolate ligand was located on the mirror plane with four of the five atoms on special positions; the central methylene carbon atom of the ligand was disordered between two positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127014. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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[17] ^{13}CN-labeling studies were carried out on the more easily purified $[(\mu\text{-edt})Fe_2(CO)_6]$ (edt = SCH_2CH_2S). IR spectra in THF solution [cm^{-1}]. Natural abundance $[(\mu\text{-edt})Fe_2(CO)_6]$: $\tilde{\nu} = \nu$(CO) 2076, 2035, 1997; $[(\mu\text{-edt})Fe_2(CO)_5CN]^-$: $\tilde{\nu} = \nu$(CN) 2097, ν(CO) 2029, 1977 + 1967, 1955 + 1943, 1916; $[(\mu\text{-edt})Fe_2(CO)_4(CN)_2]^{2-}$: $\tilde{\nu} = \nu$(CN) 2079, ν(CO) 1964, 1921, 1887. Identical solutions of [15]crown-5-solubilized KCN in THF and $K^{13}CN$ (or $KC^{15}N$) mixed with $[(\mu\text{-edt})Fe_2(CO)_6]$ in THF were monitored by IR spectroscopy. The ν(CN) band at 2097 cm^{-1} produced from KCN was displaced to 2054 cm^{-1} with $K^{13}CN$ (calcd for mass difference, 2053 cm^{-1}) and to 2068 (calcd 2064 cm^{-1}) with $KC^{15}N$. Upon further reaction with $K^{13}CN$ the identical ν(CO) band pattern and position for the natural abundance $[(\mu\text{-edt})Fe_2(CO)_4(CN)_2]^{2-}$ was observed; however, the ν(CN) band at 2079 was displaced to 2035 cm^{-1} (calcd 2035 cm^{-1}) and with $KC^{15}N$ to 2049 (calcd 2047 cm^{-1}).
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