Structure and Electronic Properties of [Ni(dsdm){Fe(CO)₃}₂], an Unusual, Triangular Nickel Diiron Compound

Marie-Cécile Chalbot,[a] Allison M. Mills,[b] Anthony L. Spek,[b] Gary J. Long,[c] and Elisabeth Bouwman*[a]

Reaction of the low-spin complex [Ni(dsdm)] with Fe_2CO_9 results in the unique trinuclear cluster [Ni(dsdm){Fe(CO)₃}₂]. NMR spectroscopy shows that the structure is diamagnetic, and, moreover, that the complex is stable in solution and C_2-symmetric. The X-ray structure reveals short distances between the distorted octahedral nickel(II) ion and the two octahedral iron(0) centers. The observed diamagnetism is explained by the formation of a triangular metal core with three two-electron two-center bonds. The Mössbauer spectra, which are typical of iron(0), are composed of asymmetric quadrupole doublets as a result of the presence of two chemically similar, but crystallographically distinct, iron sites.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

In recent years the discovery of organometallic-like fragments in the active sites of hydrogenase enzymes has given a new impetus to research pertaining to iron carbonyl chemistry. The active site of the enzyme extracted from *D. gigas* has been described as a heterodimetallic nickel-iron cluster in a sulfur-rich environment containing small diatomic CO or CN molecules coordinated to iron,[1] and the structure of the active site in the Fe-only hydrogenase isolated from *D. desulfuricans* comprises a diiron subcluster also containing CO and CN ligands.[2] Although few model compounds that properly match the active-site structure of [NiFe] hydrogenases have been reported, some do show various features of the metal coordination environment.[3−6] In spite of the research both in organometallic chemistry and in bioinorganic chemistry, the number of compounds containing both Ni and Fe bridged by a sulfur donor is rather limited.[7] Of bioinorganic interest among these are the Fe₃Ni cubane clusters and Fe₄S₄ clusters bridged to mononuclear nickel complexes, both cluster types being relevant to the active site in acetyl coenzyme-A synthase,[8,9] as well as a few heterodinuclear complexes relevant to the hydrogenase active site.[10]

In the field of organometallic cluster chemistry a huge number of structures containing the (μ-S)-Fe₂CO₆ fragment have been reported.[11] This Fe₂CO₆ fragment has recently gained renewed attention because of its importance in modeling the active site of Fe-only hydrogenases.[12] Research efforts by organometallic chemists have resulted in several complexes with a cyclopentadienylnickel unit bound to Fe(CO)₃ moieties.[13,14]

The mononuclear compound [Ni(dsdm)] {H₂dsdm = [*N,N′*-dimethyl-*N,N′*-bis(2-sulfanylethyl)ethylenediamine]} is a nickel thiolate complex used in biomimetic studies of [NiFe] hydrogenases.[15] [Ni(dsdm)] contains two *cis* sulfur atoms which are particularly reactive towards dioxygen. Indeed, the oxidation of [Ni(dsdm)] with H_2O_2 or O_2 leads to the fully oxidized [Ni(dsodm)(H₂O)₂] complex in which nickel is coordinated to the sulfonato groups.[16,17] Moreover, [Ni(dsdm)] has also been used in attempts to synthesize thiolato-bridged nickel-iron complexes. The reaction of [Ni(dsdm)] with K[HFe(CO)₄] leads to [Fe(dsdm)Ni(CO)₃]₂ and involves the reduction of nickel(II) to nickel(0) followed by the coordination of the dsdm ligand to the iron(II).[18]

We present herein the reaction of [Ni(dsdm)] with Fe₂CO₉, which results in the formation of the novel trinuclear sulfur-bridged nickel-iron complex [Ni(dsdm){Fe(CO)₃}₂], a diamagnetic compound that contains three metal centers in a compact triangular metal core.

Results and Discussion

A projection of the structure of [Ni(dsdm){Fe(CO)₃}₂] is shown in Figure 1, and the corresponding bond lengths and angles are listed in Table 1. In this trinuclear compound the Ni(dsdm) moiety coordinates to a diiron hexacarbonyl fragment and the three metals are in a nearly equilateral trian-

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, 2300 RA Leiden, The Netherlands
Fax: (internat.) +31-71/527-4451
E-mail: bouwman@chem.leidenuniv.nl
[b] Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University,
Padualaan 8, 3584 CH Utrecht, The Netherlands
[c] Department of Chemistry,University of Missouri-Rolla, Rolla, MO 65409-0010, USA

M.-C. Chalbot, A. M. Mills, A. L. Spek, G. J. Long, E. Bouwman
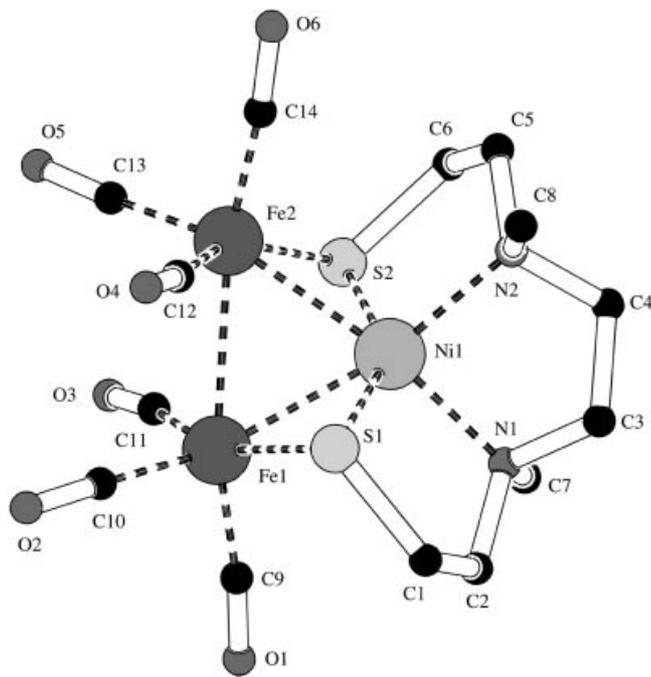
Figure 1. A PLUTON[27] projection of [Ni(dsdm){Fe(CO)$_3$}$_2$]; for clarity the hydrogen atoms have been omitted

gular arrangement with short metal-metal distances. The nickel ion is tetracoordinate to two sulfur and two nitrogen donor atoms of the dsdm ligand, in a distorted tetrahedral geometry. The two sulfur atoms each bridge the nickel ion to one of the iron tricarbonyl moieties. The dihedral angle between the planes of the two five-membered rings formed

by Ni with the N,C,C,S atoms of each sulfanylethyl portion of dsdm is 87.91(16)°, indicating a nonplanar [Ni-N$_2$S$_2$] environment. The Ni−S distances of 2.1602(11) and 2.1724(11) Å are in the range reported for the trinuclear complex [Ni$_3$(dsdm)$_2$]Cl$_2$, a complex that has pseudo-square planar nickel ions, whereas the Ni−N bond lengths of 2.061(3) and 2.077(4) Å are significantly longer.[15] If one includes the two iron centers in the coordination environment of the nickel ion, the geometry of the nickel(II) ion can be regarded as that of a distorted octahedron.

The structure contains two crystallographically distinct iron sites with small variations in the Fe−C distances and Fe−C−O angles. Each iron atom is pentacoordinate in a square-pyramidal geometry with the carbonyl C10 and C13 carbon atoms at the apex. The Fe−S bonds of 2.2553(14)−2.2567(12) Å and the Fe−C and C−O bond lengths of 1.769(4)−1.793(5) Å and 1.145(6)−1.173(5) Å, respectively, are similar to those reported for [EtS-Fe^I(CO)$_3$]$_2$.[19] The Fe−Fe bond length of 2.6618(9) Å is significantly longer than the 2.523 and 2.537 Å values found in the starting Fe$_2$CO$_9$ complex[20] and in the sulfur-bridged diiron complex [EtSFe(CO)$_3$]$_2$,[19] respectively. From structural and spectroscopic information it appears that the two Ni−Fe interactions, at distances of 2.5061(8) and 2.5131(10) Å, must be considered as metal-metal bonds. Including those in the coordination environment of the iron(0) centers, the geometry of the latter can also be regarded as that of a distorted octahedron.

At first sight it appears that a similar arrangement of nickel bridged through sulfur to Fe$_2$(CO)$_6$ fragments has been reported by Holliday et. al.[21] In the reported struc-

Table 1. Bond distances and angles in [Ni(dsdm){Fe(CO)$_3$}$_2$]

Bond distances (Å)					
Ni1···Fe1	2.5130(8)	Ni1···Fe2	2.5061(8)	Fe1···Fe2	2.6617(8)
Ni1−S1	2.1724(11)	Fe1−S1	2.2553(11)	Fe2−S2	2.2566(12)
Ni1−S2	2.1602(11)	Fe1−C9	1.781(5)	Fe2−C12	1.769(5)
Ni1−N1	2.061(3)	Fe1−C10	1.789(5)	Fe2−C13	1.794(5)
Ni1−N2	2.077(4)	Fe1−C11	1.770(4)	Fe2−C14	1.777(5)

Angles (°)					
Fe1−Ni1−Fe2	64.05(2)	Ni1−Fe1−Fe2	57.85(2)	Ni1−Fe2−Fe1	58.10(2)
Fe1−Ni1−S1	56.99(3)	Ni1−Fe1−S1	53.88(3)	Ni1−Fe2−S2	53.63(3)
Fe1−Ni1−S2	90.84(4)	Ni1−Fe1−C9	108.69(14)	Ni1−Fe2−C12	98.47(13)
Fe1−Ni1−N1	106.85(10)	Ni1−Fe1−C10	146.75(14)	Ni1−Fe2−C13	149.04(14)
Fe1−Ni1−N2	163.71(10)	Ni1−Fe1−C11	104.83(14)	Ni1−Fe2−C14	110.06(14)
Fe2−Ni1−S1	93.29(4)	Fe2−Fe1−S1	87.39(3)	Fe1−Fe2−S2	85.05(3)
Fe2−Ni1−S2	57.27(3)	Fe2−Fe1−C9	154.66(15)	Fe1−Fe2−C12	74.28(15)
Fe2−Ni1−N1	165.14(10)	Fe2−Fe1−C10	106.44(14)	Fe1−Fe2−C13	104.91(14)
Fe2−Ni1−N2	104.33(10)	Fe2−Fe1−C11	74.44(14)	Fe1−Fe2−C14	159.76(14)
S1−Ni1−S2	145.10(5)	S1−Fe1−C9	101.52(14)	S2−Fe2−C12	151.71(14)
S1−Ni1−N1	90.71(10)	S1−Fe1−C10	99.89(14)	S2−Fe2−C13	102.76(14)
S1−Ni1−N2	115.35(9)	S1−Fe1−C11	157.92(14)	S2−Fe2−C14	100.91(15)
S2−Ni1−N1	113.43(10)	C9−Fe1−C10	95.4(2)	C12−Fe2−C13	101.12(19)
S2−Ni1−N2	91.81(9)	C9−Fe1−C11	90.5(2)	C12−Fe2−C14	92.9(2)
N1−Ni1−N2	86.77(13)	C10−Fe1−C11	97.3(2)	C13−Fe2−C14	92.7(2)
Ni1−S1−Fe1	69.13(4)	Ni1−S2−Fe2	69.10(4)		
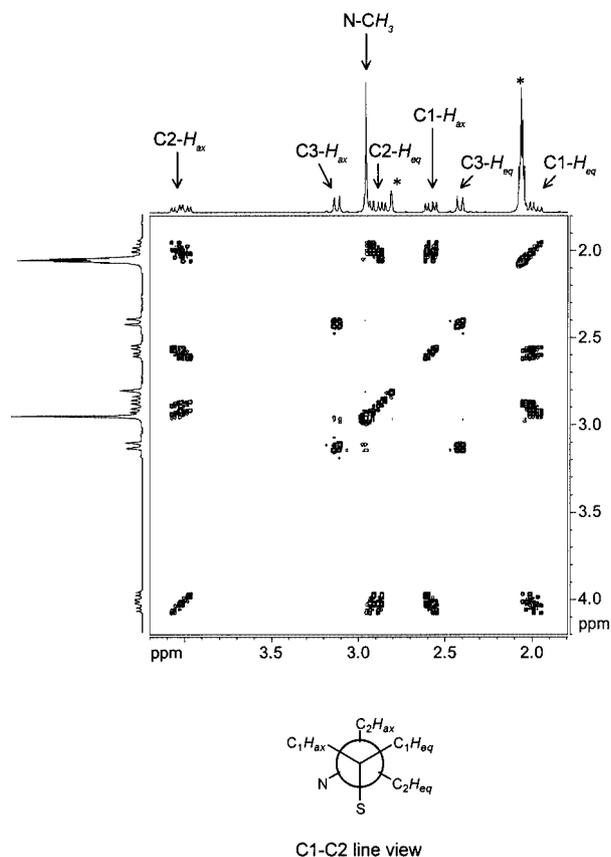
Figure 2. ^{1}H-^{1}H COSY 2D NMR spectrum of [Ni(dsdm){Fe(CO)₃}₂] at 300 MHz in [D₆]acetone; the asterisks denote signals from solvent and impurities

ture the two iron centers are bridged symmetrically by two sulfides, with a sulfur-sulfur distance of 2.83 Å, leading to a structure which, in all aspects, is more similar to the parent [(RS)Fe(CO)₃]₂ complex[19] if one includes the central NiS_4 unit as a chelating dithiolene group. In [Ni(dsdm){Fe(CO)₃}₂] the sulfur-sulfur distance in the dithiolate group formed by the tetrahedral Ni(dsdm) unit is too large (4.13 Å) for each sulfur to bind both Fe atoms; thus a $FeSC_3$ chromophore rather than the typical FeS_2C_3 chromophore is observed. The resulting electron deficiency of the iron center in [Ni(dsdm){Fe(CO)₃}₂] is compensated for by the additional Ni−Fe interactions. The total electron count of the trinuclear cluster is 48, similar to $Fe_3(CO)_{12}$.

[Ni(dsdm){Fe(CO)₃}₂] is diamagnetic and has been characterized by ^{1}H and ^{13}C NMR spectroscopy in solution. The NMR spectrum exhibits six sharp multiplets and a singlet, which have been assigned to the aliphatic hydrogens by ^{1}H-^{1}H COSY 2-D NMR spectroscopy (Figure 2). The presence of only seven signals indicates that, in solution, the two iron atoms are equivalent. The diamagnetism of the compound arises through the formation of a triangular metal core with three two-electron two-center bonds.

The Mössbauer spectra of [Ni(dsdm){Fe(CO)₃}₂] obtained at 80 and 297 K are shown in Figure 3. The spectra are composed of asymmetric doublets as a result of the presence of two chemically similar, but crystallographically distinct, iron sites. The spectra have been fitted at a given temperature with two quadrupole doublets both with the same line-width and area.

In Table 2 a comparison of the hyperfine parameters observed for [Ni(dsdm){Fe(CO)₃}₂] with those of other {Fe(CO)₃}₂ adducts such as ([Fe(CO)₃NH₂]₂, [Fe(CO)₃SMe]₂, and [Fe(CO)₃SPh]₂) is given, revealing the similarity of the chemical bonding found in these adducts.[22−24] In contrast, the hyperfine parameters of [Ni(dsdm){Fe(CO)₃}₂] are significantly different from those reported for Fe₂(CO)₉.[25] In all cases the adduct coordin-
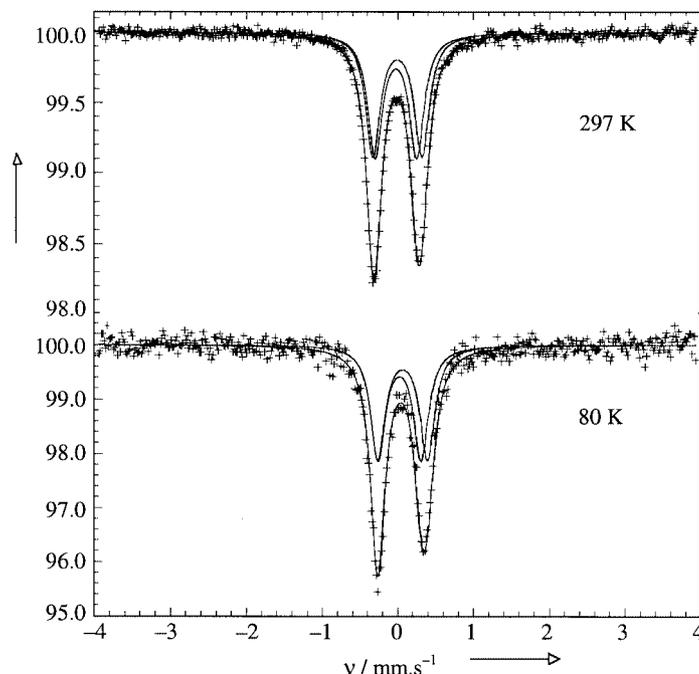

Figure 3. The Mössbauer spectra of [Ni(dsdm){Fe(CO)₃}₂] obtained at 80 and 297 K

Table 2. Mössbauer spectroscopic hyperfine parameters for [Ni(dsdm){Fe(CO)$_3$}$_2$] and related {Fe(CO)$_3$} adducts

Compound	T (K)	δ (mm/s)[a]	ΔE$_Q$ (mm/s)	Γ (mm/s)	Area (%)	Ref
[Ni(dsdm){FeCO$_3$}$_2$]	297	−0.005	0.65	0.23[b]	50[b]	[c]
		−0.025	0.55	0.23[b]	50[b]	[c]
	80	0.066	0.66	0.23[b]	50[b]	[c]
		0.027	0.57	0.23[b]	50[b]	[c]
[Fe(CO)$_3$NH$_2$]$_2$,	80	0.02	0.85	−	−	[22]
syn-[Fe(CO)$_3$SMe]$_2$	80	0.03	1.00	−	−	[23]
anti-[Fe(CO)$_3$SMe]$_2$	80	0.03	0.88	−	−	[23]
[Fe(CO)$_3$SPh]$_2$	80	0.06	1.07	−	−	[24]
Fe$_2$CO$_9$	80	0.17	0.42	−	−	[25]

[a] The isomer shifts are given relative to room temperature α-iron foil. [b] These parameters were constrained to be equivalent at a given temperature. [c] This work.

ated to the iron center has reduced the isomer shift relative to that found in Fe$_2$(CO)$_9$. This reduction corresponds to the expected increase in the s-electron density at the iron-57 nucleus. Furthermore, the quadrupole splittings observed for [Ni(dsdm){Fe(CO)$_3$}$_2$] are intermediate between those of the other adducts and Fe$_2$(CO)$_9$, indicating that the presence of S1 and S2 coordinated to Fe$_2$(CO)$_6$ in [Ni(dsdm){Fe(CO)$_3$}$_2$] has reduced the electronic asymmetry at the iron site, but to a lesser extent than is found in Fe$_2$(CO)$_9$.

Conclusion

To supplement the large number of organometallic clusters containing the Fe$_2$(CO)$_6$ fragment that have been reported, we have described herein the first cluster in which additional Ni−Fe metal-metal bonds are present. The unique nature of [Ni(dsdm){Fe(CO)$_3$}$_2$] is related to the atypical binding of the two thiolate sulfurs to the Fe$_2$(CO)$_6$ fragment, resulting in short distances between the octahedral, high-spin nickel(II) ion and the two octahedral iron(0) centers. This remarkable structure provides an additional, interesting example of the structural versatility possible for the reaction products formed from the nickel *cis* thiolate complex [Ni(dsdm)]. For comparison, the reaction of the related, but more rigid, [Ni(bme-daco)] complex with Fe$_2$CO$_9$ produces a dinuclear nickel-iron tetracarbonyl compound, in which the nickel(II) ion remains low-spin in a square-planar environment.[10]

Experimental Section

General Remarks: [Ni(dsdm)] was synthesized according to standard procedures.[15] The Mössbauer spectra were measured at 80 and 297 K on a constant-acceleration spectrometer, which utilized a room temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with α-iron foil. The spectra were fitted as two symmetric quadrupole doublets and the estimated absolute errors are ± 0.005 mm·s^{-1} for the isomer shifts, ± 0.01 mm·s^{-1} for the quadrupole splittings and line widths, and ± 0.02 (%ε) (mm·s^{-1}) for the absolute spectral areas. UV/Vis-NIR measurements were performed on a Perkin−Elmer Lambda 900 UV/Vis/

NIR spectrometer. IR spectra were recorded on a Perkin−Elmer FT-IR Paragon 1000 spectrometer. ^{1}H, ^{13}C, and ^{1}H−^{1}H 2D COSY NMR spectra were recorded on a Bruker 300 DPX MHz spectrometer. Elemental analyses were performed with a Perkin−Elmer series II CHNS/O analyzer 2400.

[Ni(dsdm){Fe(CO)$_3$}$_2$]: The preparation was carried out in dry degassed solvent under an argon atmosphere by using standard Schlenk techniques. Fe$_2$CO$_9$ (0.357 g, 1 mmol) was added to a suspension of [Ni(dsdm)] (0.265 g, 1 mmol) in 10 mL of toluene. The reaction mixture was stirred for 48 hours, during which time the toluene solution developed a dark-brown color. The toluene solution was filtered to remove the insoluble material. Crystals suitable for X-ray crystallography were obtained from toluene/hexane two-layer crystallization within one day (yield 0.60 g, 11%). Attempts to optimize the yield were not undertaken. UV/Vis (CH$_3$CN): λ$_{max}$ (ε) = 1007 (50), 495 (shoulder), 394 (5150) nm. IR (diamond): ν(CO) = 2009, 1956, 1917, 1900, and 1885 cm^{-1}. C$_{14}$H$_{18}$Fe$_2$N$_2$NiO$_6$S$_2$: calcd. 30.86, H 3.33, N 5.14, S 11.77, Ni 10.77, Fe 20.50; found C 30.99, H 3.49, N 5.30, S 11.00, Ni 10.70, Fe 19.94. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 4.02 (m, 2 H, C2-H_{ax}), 3.13 (d, 2 H, C3-H_{ax}), 2.96 (s, 6 H, N-CH_3), 2.91 (m, 2 H, C2-H_{eq}), 2.58 (dd, 2 H, C1-H_{ax}), 2.42 (d, 2 H, C3-H_{eq}), 1.99 (m, 2 H, C1-H_{eq}) ppm. ^{13}C NMR (300 MHz, CDCl$_3$): δ = 214 (C=O), 60 (*C3*), 54 (*C2*), 51 (CH_3), 38 (*C1*).

X-ray Crystallographic Study: C$_{14}$H$_{18}$Fe$_2$N$_2$NiO$_6$S$_2$, M_r = 544.83, dark purple rectangular plates (0.05 × 0.12 × 0.24 mm), monoclinic, P2$_1$/c, a = 9.7562(2), b = 13.9094(4), c = 17.2651(4) Å, β = 121.0760(13)°, V = 2006.68(9) Å^3, Z = 4, ρ$_c$ = 1.803 g·cm^{-3}, μ = 2.595 mm^{-1}; intensity data were collected on a Nonius Kappa CCD diffractometer with rotating anode (Mo-$K_α$, λ = 0.71073 Å) at 150 K to a maximum resolution of θ$_{max}$ = 27.5°, 20667 measured reflections, 4588 unique reflections, 3081 observed data [$I > 2.0\sigma(I)$], R_{int} = 0.060; convergence was reached at R1 [$I > 2.0\sigma(I)$] = 0.0421, wR2 = 0.0934, and S = 1.08 for 4588 reflections and 246 parameters, Δρ$_{max/min}$ = 0.49/−0.54 e·Å^{-3}. The structure was solved by direct methods using SHELXS-97[26] and refined on F^2 using SHELXL-97; an empirical absorption correction was applied using DELABS in PLATON[27] (0.589−0.876 transmission); geometrical calculations and molecular graphics preparation were performed with PLATON; all non hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atom were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. CCDC-184378 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at

www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[1] A. Volbeda, M. H. Charon, C. Piras, E. C. Hatchikian, M. Frey, J. C. Fontecilla-Camps, *Nature* **1995**, *373*, 580−587.

[2] Y. Nicolet, C. Piras, P. Legrand, E. C. Hatchikian, J. C. Fontecilla-Camps, *Struct. Fold. Des.* **1999**, *7*, 13−23.

[3] J. C. Fontecilla-Camps, *J. Biol. Inorg. Chem.* **1996**, *1*, 91−98.

[4] M. Y. Darensbourg, E. J. Lyon, J. J. Smee, *Coord. Chem. Rev.* **2000**, *206−207*, 533−561.

[5] R. B. King, T. E. Bitterwolf, *Coord. Chem. Rev.* **2000**, *206−207*, 563−579.

[6] A. C. Marr, D. J. E. Spencer, M. Schroder, *Coord. Chem. Rev.* **2001**, *219−221*, 1055−1074.

[7] A search in the Cambridge Structural Database for Ni−S−Fe resulted in only 30 independent hits.

[8] J. Zhou, M. J. Scott, Z. Hu, G. Peng, E. Münck, R. H. Holm, *J. Am. Chem. Soc.* **1992**, *114*, 10843−10854.

[9] F. Osterloh, W. Saak, S. Pohl, *J. Am. Chem. Soc.* **1997**, *119*, 5648−5656.

[10] C.-H. Lai, J. H. Reibenspies, M. Y. Darensbourg, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2390−2393.

[11] A search in the Cambridge Structural Database for (CO)₃Fe−S−Fe(CO)₃ resulted in over 350 hits.

[12] E. J. Lyon, I. P. Georgakaki, J. H. Reibenspies, M. Y. Darensbourg, *Angew. Chem. Int. Ed.* **1999**, *38*, 3178−3180.

[13] P. Braunstein, E. Sappa, A. Tiripicchio, M. Tiripicchio Camellini, *Inorg. Chim. Acta* **1980**, *45*, L191−L193.

[14] L.-C. Song, Y.-B. Dong, Q.-M. Hu, X.-Y. Huang, J. Sun, *Organometallics* **1997**, *16*, 4540−4545.

[15] M. A. Turner, W. L. Driessen, J. Reedijk, *Inorg. Chem.* **1990**, *29*, 3331−3335.

[16] R. K. Henderson, E. Bouwman, A. L. Spek, J. Reedijk, *Inorg. Chem.* **1997**, *36*, 4616−4617.

[17] V. E. Kaasjager, E. Bouwman, M. Y. Darensbourg, A. Derecskei-Kovacs, S. Gorter, C. A. Grapperhaus, J. Reedijk, J. H. Reibenspies, J. J. Smee, L. M. Thomson, *Inorg. Chem.* **2002**, *41*, 1837−1844.

[18] E. Bouwman, R. K. Henderson, A. L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* **1999**, 217−219.

[19] L. F. Dahl, C.-H. Wei, *Inorg. Chem.* **1963**, *2*, 328−333.

[20] F. A. Cotton, J. M. Troup, *J. Chem. Soc., Dalton Trans.* **1974**, 800−802.

[21] R. L. Holliday, L. C. Roof, B. Hargus, D. M. Smith, P. T. Wood, W. T. Pennington, J. W. Kolis, *Inorg. Chem.* **1995**, *34*, 4392−4401.

[22] R. B. King, L. M. Epstein, E. W. Gowling, *J. Inorg. Nucl. Chem.* **1970**, *32*, 441−445.

[23] J. P. Crow, W. R. Cullen, F. G. Herring, J. R. Sams, R. L. Tapping, *Inorg. Chem.* **1971**, *10*, 1616−1623.

[24] E. Kostiner, A. G. Massey, *J. Organomet. Chem.* **1969**, *19*, 233−236.

[25] K. Farmery, M. Kilner, R. Greatrex, N. N. Greenwood, *J. Chem. Soc. A* **1969**, 2339−2345.

[26] G. M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen (Germany) **1997**.

[27] A. L. Spek, PLATON, A multipurpose crystallographic tool, Utrecht University (The Netherlands) **2002**.