A Sulfido-Bridged Diiron(II) Compound and Its Reactions with Nitrogenase-Relevant Substrates

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The iron–molybdenum cofactor (FeMoco, Figure 1a) is the site at which nitrogenase reduces N_2, small nitriles, isocyanides, and alkynes.[1] Recent X-ray studies suggest the presence of a central atom X (X = C, N, or O) in the center of the FeMoco;[2,3] six "belt" iron atoms have trigonal pyramidal geometries (see below) with X in the axial positions. These symmetrically disposed iron atoms are implicated in reactivity by ab initio calculations,[3] the spectroscopy and activity of mutants,[4] and the comparable activity of iron-only nitrogenases.[1,5] Because X does not interact strongly with the "belt" iron atoms,[6,7] and X is hypervalent, it is likely that Fe–X bonds are disrupted during catalysis.[3e] Three-coordinate iron complexes therefore mimic possible reactive forms of the FeMoco with broken Fe–X bonds. However, synthetic iron–sulfur clusters containing three-coordinate iron are not known.[8] Very few complexes with three-coordinate iron have sulfur ligands, and their reactivity has not been reported.[9] Here, we report a low-coordinate, sulfide-bridged diiron complex that resembles a fragment of the FeMoco belt and describe its reactivity toward nitrogenase-relevant substrates.

Addition of sulfur to $[(LFe)_2(\mu-N_2)]$[10] (L = [HC(CMeN[2,6-diisopropylphenyl])$_2$]⁻) in diethyl ether gave the dinuclear diiron-(II) sulfide LFeSFeL (1) (Figure 1b) in 82% yield. The crystal structure of 1 reveals that the molecule is highly bent at the bridging atom (Fe–S–Fe = 101.70(7)°). The FeSFe core has Fe–S bond distances of 2.250(2) and 2.346(2) Å. Iron atoms bridged by a single sulfide are known only in a few FeS clusters and in five-coordinate species.[11,12] The 4.2 K zero-field Mössbauer spectrum of 1 in benzene exhibits a single quadrupole doublet with $\Delta E_Q = 0.58$ mm/s and isomer shift $\delta = 0.86$ mm/s; spectra recorded in applied fields up to 7.0 T show that the two Fe(II) ions are antiferromagnetically coupled to give a diamagnetic ground state (for details on X-ray structures and Mössbauer spectra of 1, see the Supporting Information).[13]

Compound 1 is stable under dry nitrogen, but forms adducts with nitrogen donors. In C_6D_6 solution, acetonitrile binds to 1 ($K_{assoc} = 340 \pm 60$ M⁻¹), with rapid exchange on the NMR time scale. The binding is 1:1, as shown by an NMR titration (Figure 2a) and the crystal structure of the adduct (1·CH₃CN). Compound 1·CH₃CN (Figure 2b) contains three- and four-coordinate iron atoms in close proximity (Fe–Fe = 3.8365(9) Å). The three-coordinate iron in 1·CH₃CN does not interact with the nitrile triple bond. Methylhydrazine and 1,1-dimethylhydrazine bind end-on to the sulfide in a 2:1 ratio (Figures 3a and S-2). Hydrazine-bound species have been postulated as part of the catalytic cycle of nitrogenase.[14] Ammonia binds to the sulfide to form 1·2NH₃, with a structure like that of the other 2:1 adducts (Figure S-2).

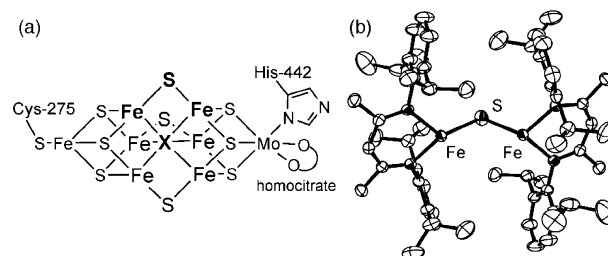† University of Rochester.
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Figure 1. (a) FeMoco of nitrogenase.[2] (b) Molecular structure of 1 (50% ellipsoids, H atoms omitted). The sulfide bridge is shown in one of the two half-occupancy, symmetry-equivalent bridging positions. See the Supporting Information for structural details.
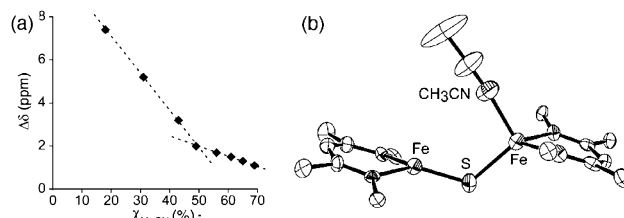

Figure 2. (a) Job plot for CH₃CN binding to 1 in C_6D_6. (b) Molecular structure of 1·CH₃CN (50% ellipsoids, H and aryl groups omitted).
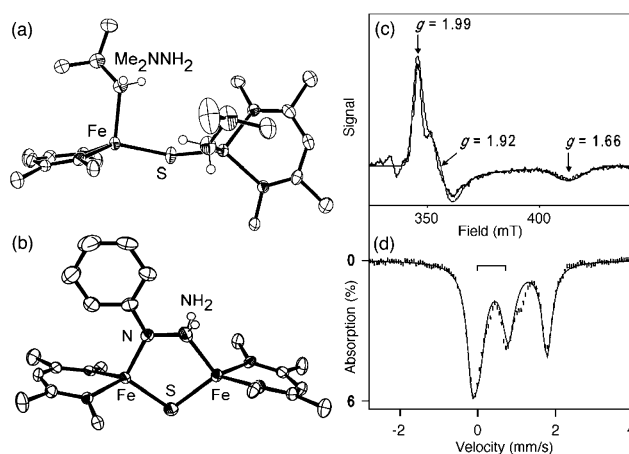

Figure 3. Molecular structures of (a) 1·2Me₂NNH₂ and (b) 2 (50% ellipsoids, C-bound H atoms and aryl groups omitted). (c) X-band EPR spectrum (toluene, 9 K, 9.622 GHz) of 2, with $S = \frac{1}{2}$ simulation. (d) Mössbauer spectrum of 2 (solid, 140 K), with simulation for two doublets (representing 86% of the total Fe) using parameters quoted in the text. The bracket indicates the doublet for the ferric site, and the shoulder at +0.8 mm/s belongs to a contaminant (14%).

In constrast, treatment of 1 with phenylhydrazine gave the mixed-valence Fe^{II}Fe^{III} complex 2, which was formed in ∼90% yield and isolated in 41% yield. Its crystal structure (Figure 3b) shows that 2 contains a formally anionic, bridging phenylhydrazido ligand.

Table 1. Geometric Parameters

compound	Fe···Fe (Å)	Fe–S–Fe (deg)	τ^a
1	3.5644(9)	101.70(7)	
1·CH₃CN	3.8365(9)	119.25(10)	0.16
2	3.4498(9)	101.50(6)	0.19 Fe^{III}
			0.10 Fe^{II}
1·2Me₂NNH₂	4.1864(9)	141.91(5)	0.31
1·2NH₃	3.9782(7)	126.56(5)	0.33
1·2MeNHNH₂	4.1158(10)	136.53(8)	0.48
FeMoco²	2.60(2)	71.2(4)	0.46
basket clusters¹¹	2.6–2.8	74–76	0.8–1.0
[(ⁱPrNCOCH₂)₃N)Fe]⁻ ¹⁷			1.18

$^a \tau = [\Sigma(\angle L_{basal}-Fe-L_{basal}) - \Sigma(\angle L_{basal}-Fe-L_{axial})]/90$. See the Supporting Information for details.

The negative charge on the ligand is evident from the planar α-nitrogen (sum of angles $359.9 \pm 1.0°$). The rhombic EPR spectrum (Figure 3c) suggests an antiferromagnetically coupled system with an $S = {}^1/_2$ ground state. The Mössbauer spectrum (Figure 3d) of solid **2** reveals valence-trapped iron(II) ($\Delta E_Q = 1.93$ mm/s, $\delta = 0.82$ mm/s) and iron(III) ($\Delta E_Q = 0.74$ mm/s, $\delta = 0.41$ mm/s) sites (Figure 3c). Studies in applied fields up to 7.0 T show that the components of the ^{57}Fe magnetic hyperfine tensors of the ferric and ferrous sites are negative and positive, respectively, consistent with antiferromagnetic coupling.[15]

Interestingly, the reaction that gives **2** requires 1.4 ± 0.2 equiv of phenylhydrazine, and aniline (GC/MS) and ammonia (up to 0.5 equiv detected by the indophenol method) are produced. A balanced equation for the formation of **2** consistent with these observations is shown in eq 1.

$$2(\mathbf{1}) + 3PhNHNH_2 \rightarrow 2(\mathbf{2}) + PhNH_2 + NH_3 \qquad (1)$$

Therefore, N–N single bonds are cleaved by the diiron(II) sulfide complex. Cleavage of hydrazine N–N bonds is well-known for metals in groups 4–6,[16] and some ruthenium examples exist,[16c] but there is only one example for iron.[16d] Interestingly, Fe₃MoS₄ clusters catalytically reduce hydrazine, but the Fe₄S₄ analogues are inactive.[16e]

Because the key "belt" sites of the FeMoco appear to be distorted from tetrahedral toward a trigonal pyramidal[17] geometry, it is of interest to quantify pyramidal distortions of tetrahedral iron(II) in these synthetic compounds. In Table 1, we introduce a normalized measure of pyramidalization τ, which describes the distortion of tetrahedral coordination along a pseudo-C_3 axis ($\tau = 0$ for tetrahedron, $\tau = 1$ for trigonal pyramid with flat base). As expected, the FeMoco belt iron atoms are fairly pyramidalized ($\tau = 0.46 \pm 0.03$). The iron sites in FeS clusters are tetrahedral ($\tau \leq 0.3$), except for the "basket" clusters and close relatives (see the Supporting Information).[11] The iron atoms in **1·CH₃CN** and **2** are nearly tetrahedral ($\tau = 0.10–0.19$), but the alkylhydrazine and ammonia adducts of **1** are substantially pyramidalized ($\tau = 0.31–0.48$).

Thus, the belt iron atoms of FeMoco have significant pyramidal distortion, and this work shows that comparable distortions can be achieved in synthetic complexes without the aid of constraining ligands. The adducts of **1** have τ values that do not correlate with ligand size, suggesting that pyramidalization may be electronically controlled. The diketiminate-supported FeSFe core is quite flexible, with Fe···Fe distances ranging from 3.45 to 4.19 Å and Fe–S–Fe angles varying from 101.5° to 141.9°. Theoretical studies indicate that diketiminate ligands have "soft" electronic properties commonly associated with sulfide/thiolate ligands.[13,18] Because the synthetic sulfide complex described here binds nitrogen donors and cleaves

N–N bonds, it shows great promise for mimicking key features of biological nitrogen fixation.

Supporting Information Available: Synthetic, characterization, structural, binding, and spectroscopic data (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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