A Sulfide-Bridged Diiron(II) Complex with a N₂H₄ Ligand

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Abstract. A sulfide-bridged diiron(II) complex bearing a *cis*-N₂H₄ (hydrazine) ligand has been prepared by reaction of LFe^{II}(μ -S)Fe^{II}L (1; L = sterically encumbered β -diketiminate ligand) with 2 molar equivalents of N₂H₄. The metastable diiron(II) hydrazine complex LFe^{II}(μ -S)(μ -H₂N–NH₂)Fe^{II}L (3) is formed, as shown by crystallography, NMR, vibrational, and electronic absorption spectroscopy.

Introduction

Coordination chemistry has its roots in the work of *Werner*, which was recognized by a Nobel Prize 100 years ago in 1913.^[1] Coordination chemistry relevant to biological systems now represents a dynamic subdiscipline of coordination chemistry.^[2] One challenge in bioinorganic chemistry is biological dinitrogen reduction (Equation (1)),

$$N_2 + 8 e^- + 8 H^+ \rightarrow 2 NH_3 + H_2$$
 (1)

which is best characterized at the iron-molybdenum cofactor (FeMoco, Figure 1) of nitrogenase enzymes.^[3] Likely intermediates include hydrazine (H₂N–NH₂) and its short-lived partner diazene (HN=NH), which are also substrates for nitrogenase.^[3,4] Recent studies have trapped adducts (or products) from N₂, HN=NCH₃, and N₂H₄ on the FeMoco.^[5]



Figure 1. Structural similarity between a portion of the FeMoco of nitrogenase (left) and complex 1 (right).

Progress in understanding the structure and reactive states of FeMoco has been facilitated through spectroscopic studies on model complexes and enzymes.^[3–6] The FeMoco in its resting state has an intriguing six-coordinate carbide ion at its center (Figure 1),^[7] and ¹⁴C tracer studies indicate that the carbide

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Compound **3** has been crystallographically characterized as its DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) adduct, which exhibits weak N–H…DBU hydrogen bonding. The synthetic process evolves roughly 2 equivalents of NH₃. The *cis*-N₂H₄ bridge in **3** may be relevant to the structure and function of intermediates on the FeMoco of nitrogenase.

does not exchange during catalytic turnover.^[8] This suggests that the central carbide may function as a hemilabile ligand, in which some bonds are reversibly broken upon reductive activation of the cofactor.^[6a,9] It is therefore reasonable to hypothesize that substrate binding occurs at one or more low-coordinate iron atoms bonded directly to a bridging sulfide ligand. This idea could be supported by understanding of the binding modes and behavior of N₂H_x fragments on well-characterized multi-iron sulfide complexes. Work by *Sellmann* established the complexation of hydrazine and diazene in iron complexes,^[9a] and more recent progress has come from study of additional mononuclear and dinuclear iron complexes with parent N₂H₄ ligands.^[10,11]

We previously reported the reactivity of a sulfide-bridged diiron(II) complex (1) with ammonia and with substituted hydrazines.^[12] Addition of H₂NNR₂ (R = alkyl) gave isolable Lewis base adducts, while addition of phenylhydrazine afforded a mixed-valence Fe^{II}Fe^{III} complex (2).^[12] Formation of **2** required two equivalents of **1** for every three PhNHNH₂ consumed, generating one equivalent each of NH₃ and PhNH₂ (Scheme 1). Herein, we report the reaction of **1** with the parent N₂H₄, which releases NH₃ and forms a DBU-stabilized diiron(II) complex of bridging hydrazine (**3·DBU**). To the best



Scheme 1. Previously reported reactions of 1 with substituted hydrazines, including the formation of complex 2.^[12]

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SHORT COMMUNICATION

of our knowledge, **3** is the first sulfide-bridged diiron complex of N_2H_4 .^[13] Because **3** has a low-coordinate iron-sulfide core that resembles a part of the FeMoco, study of its structure and spectroscopic features is an important step in defining the possible geometries of iron-hydrazine adducts during N_2 reduction.

Results and Discussion

In an improved synthesis, complex **1** was synthesized from Me₃P=S and 2 equiv. of a three-coordinate iron(II) β -diketiminate isobutyl complex in 89% yield (Ar = 2,6-diisopropylphenyl), as described in the Experimental Section.^[14] When **1** is treated with at least 2 equiv. of hydrazine in [D₈]THF at 0 to 30 °C, a red solution instantly forms with new ¹H NMR signals consistent with **3** (Scheme 2). Addition of excess N₂H₄ has no observable effect on product formation (leading only to more rapid decomposition of **3**), and addition of less than 2 equiv. of N₂H₄ to **1** gives partial conversion to **3**. The lifetime of **3** in solution is relatively short ($t_{1/2} \sim 30$ min at 25 °C in C₆D₆, toluene, THF, or Et₂O), with ¹H NMR and UV/Vis spectroscopic data showing decomposition to unidentified, insoluble products. This rapid decomposition prevented full characterization of **3** by elemental analysis.



Scheme 2. Formation of 3, which is crystallized as 3 DBU. DBU forms a hydrogen bond to 3 in the solid-state structure, but does not bind strongly in solution.

A single crystal of **3·DBU** was obtained by allowing an Et₂O solution of **1**, hydrazine, and DBU (1,8-diazabicycloundec-7-ene) to stand at -38 °C (Scheme 2). The major conformer in the X-ray crystallographic structure is shown in Figure 2. Complex **3·DBU** is a rare example of a crystallographically characterized sulfide-bridged N₂H₄ complex,^[15] and the only such diiron complex.^[16] The solid-state structure displays an Fe…Fe distance of 3.5960(7) Å, and the Fe–S–Fe angle of 105.68(4)° is similar to those in other sulfide-bridged diiron complexes.^[12,17] Previous diiron hydrazine complexes exhibit Fe–N_{hydrazine} distances of 2.02–2.25 Å and N–N distances of 2.231(13) and 2.163(6) Å are similar. The asymmetry in the Fe–N_{hydrazine} bond lengths is also similar to literature hydrazine complexes.^[14]

The X-ray structural data for **3-DBU** fit well to a superposition of two conformers, which could be modeled adequately. In order to model this disorder, the N–N distances in each conformer were restrained to be similar and therefore should be viewed with some caution, though the average refined N–N bond length of 1.434(13) Å is similar to those in



Figure 2. Thermal-ellipsoid plot (50% probability) of *cis*-hydrazine diiron(II) complex **3·DBU**. Carbon-bound hydrogen atoms, isopropyl groups of ligand, and DBU omitted for clarity. There is disorder in the bridging N_2H_4 ligand, and the major conformation is shown.

the literature for bridging hydrazines.^[18] In the few known diiron hydrazine adducts, a *cis* coordination geometry is particularly rare,^[13,18,10b] and the solid-state structure of the tris(phosphanyl)borate-supported low-spin diiron(II) complex exhibits an N–N_{hydrazine} distance of 1.465(3) Å. The Fe–N–N angles in **3·DBU** are each roughly 112°, consistent with sp³ hybridization about N in the N₂H₄ ligand. Complex **3** also exhibits UV/Vis (λ_{max} 497 nm; ε = 3700 M⁻¹ cm⁻¹) and highly symmetrical ¹H NMR spectra at 25 °C, consistent with the assigned structure.

Infrared spectra of **3** showed a v_{N-H} band at 3361 cm⁻¹ that is shifted to 2490 cm⁻¹ in **3-***d*₄ (formed in an analogous fashion from **1** and N₂D₄). This N–H stretching frequency is shifted from that in free N₂H₄, which exhibits a single band centered at approx. 3300 cm⁻¹. Related hydrazine complexes (and their isotopomers) display similar IR absorptions between 3398 and 3139 cm⁻¹.^[10]

It is important to note that formation of the characteristic ¹H NMR resonances of **3** was independent of the presence or absence of DBU. These experiments suggest that this base does not play a significant role in forming **3**, and does not bind strongly to **3** in solution. However, a hydrogen bond between hydrazine and DBU is clearly present in crystalline **3**·DBU, with an N···N distance of 2.91(2) Å. Thus, we surmise that its role is limited to enabling the packing of **3**·DBU into single crystals.

The requirement for more than 1 equiv. of hydrazine during the formation of **3** suggested that some of the hydrazine might be reduced to ammonia, as previously observed during the formation of **2**.^[12] Thus, a toluene solution of **1** was treated with \geq 2 equivalents of N₂H₄ (with or without DBU) at 25 °C in a sealed vessel, followed by vacuum distillation of volatile materials onto a degassed solution of 1.0 M HCl in Et₂O at -78 or -196 °C. The NH₄Cl formed was weighed to determine the



yield of NH₃. In smaller scale reactions, ¹H NMR spectra of NH₄Cl solutions in [D₆]DMSO were used to integrate the amount of recovered ammonia vs. an internal mesitylene integration standard.^[19] Each method indicated the presence of 1.7 ± 0.3 equiv. of NH₄Cl per mole of **1**. Because we were unable to isolate significant quantities of **3** or **3**·DBU in pure form, we were unable to determine whether the approx. 2 equiv. of ammonia arose during the formation of **3** or from subsequent degradation of **3**. Therefore, the full stoichiometry of the formation of **3** (Scheme 2), its decomposition pathway, and the source of electrons for the hydrazine reduction remain unknown.

The poor solubility of hydrazine in suitable solvents and extremely rapid formation of **3** hindered studies to determine the mechanism through which complex **3** is formed. However, we note that neither 1,4-cyclohexadiene (up to 1 M) nor BHT (up to 50 mM) has a discernible effect on the formation of **2** or **3**, suggesting the absence of free radicals. Also, the presence or absence of DBU gave no appreciable differences in the lifetime of **3**, as measured by UV/Vis and ¹H NMR spectroscopy.

Conclusions

A sulfide-bridged hydrazine complex **3** has been generated by addition of N_2H_4 to a low-coordinate, sulfide-bridged diiron(II) complex and characterized by X-ray crystallography, as well as by ¹H NMR and FT-IR spectroscopy. This is relevant to biological N_2 reduction, by showing that N_2H_4 can be cooperatively bound by two nearby Fe atoms with a sulfide bridge, and providing metrical and spectroscopic details on this type of compound.

Experimental Section

General Considerations: All manipulations were performed under N2 or Ar atmosphere via standard Schlenk techniques or in an inert atmosphere glovebox maintained at < 2 ppm O₂ and < 2 ppm H₂O. Unless otherwise noted, NMR spectra were recorded on a 500 MHz Bruker Avance spectrometer at 20 °C, and are referenced to residual solvent peaks. Infrared data were recorded using a Shimadzu FT-IR 8400S spectrometer. Electronic absorption spectra were recorded using a Cary 50 UV/Vis spectrophotometer using quartz cuvettes with a screw cap. Low-temperature ($T \ge -60$ °C) and in situ-added N₂H₄ experiments were conducted in quartz cuvettes fused to a resealable glass extension bearing a sidearm valve and a ground glass joint sealed with a rubber septum or glass stopper. Excess N₂H₄ was added via cannula syringe (loaded in the glovebox) as a neat reagent. FT-IR spectroscopic studies were conducted using thin films cast onto NaCl plates from concentrated Et₂O solutions (or the aforementioned reaction media) immediately prior to data collection. Anhydrous hydrazine (Aldrich) was degassed using three freeze-pump-thaw cycles, and then dried by passage through a plug of activated alumina in the glove box. Solvents were dried with Na/benzophenone and/or by passage through a column (Glass Contour Co., Laguna Beach, CA) or plug of activated alumina under N₂ atmosphere and stored in the glovebox. Celite was dried at 200 °C under vacuum overnight. Trimethylphosphine sulfide was prepared in quantitative yield by adding a slight excess of a 1.0 M toluene solution of trimethylphosphine to a rapidly stirred solution of elemental sulfur dissolved in toluene under an N2 atmosphere while

cooling in a 0 °C bath, then allowing the solution to warm to 20 °C overnight.^[20] L^{Me}Fe*i*Bu,^[21] HL^{Me},^[22] [L^{Me}Fe(μ -Cl)]₂,^[23] FeCl₂(THF)_{1.5}^[24] were prepared according to literature procedures. L^{Me} refers to the 2,4-bis(2,6-diisopropylphenylimido)pentyl anion.

 $L^{Me}Fe(\mu-S)FeL^{Me}$ (1): A 100 mL resealable flask was charged with a magnetic stir bar, $L^{Me}FeiBu$ (480 mg, 0.905 mmol), and toluene (15 mL). To this solution was slowly added a toluene solution (15 mL) of Me₃PS (213 mg, 1.97 mmol) over 2–3 min while stirring at 25 °C. The dark red-brown solution was heated in a 100 °C oil bath for 24 h. Volatile materials were removed in vacuo at 25 °C, leaving a brown residue. The solids were taken up in pentane (20 mL), and the resulting brown solution was filtered through a Celite pad and evacuated to dryness. Crystallization from pentane or 4:1 pentane:(Me₃Si)₂O mixture (ca. 15 mL) affords 1 as a crystalline burgundy solid in 89.2% yield (395 g, 0.403 mmol). The spectroscopic properties agree with literature values.^[12]

 $L^{Me}Fe(\mu-S)(\mu-N_2H_4)FeL^{Me}$ (3): This complex was prepared in situ or immediately prior to spectroscopic studies because of its decomposition within minutes at room temperature. In NMR scale experiments, the purity of up to 1.0 mL of a 5–20 mM solution of 3 in [D₆]benzene, [D₈]toluene, or [D₈]THF was verified by ¹H NMR spectroscopy in a J. Young NMR tube containing a sealed capillary tube holding an internal standard solution (typically L'^{Bu}FeCl in [D₈]toluene). In the glovebox, neat N_2H_4 (ca. 1–100 µL) was added by microsyringe to the wall of the NMR tube, taking care to prevent mixing with the solution of 3. The sample was then shaken immediately before freezing or ¹H NMR spectroscopic observations. ¹H NMR spectra at 25 °C were similar in C_6D_6 (Figure S1) and $[D_8]$ THF (Figure S2), and are most consistently assigned as $\delta = 10$ (6 H, backbone CH₃), 7.2 (4 H, isopropyl CH(CH₃)₂ or m-Ar), -1.4 (2 H, p-Ar), -2.3 (12 H, isopropyl CH(CH₃)₂), -7 (4 H, isopropyl CH(CH₃)₂ or m-Ar), -14 (1 H, backbone CH), -24 (12 H, isopropyl CH(CH₃)₂) ppm (all broad singlets). The assignments are not definitive, due to overlap with peaks from decomposition products (identified in Figures S1 and S2). FT-IR (thin film on NaCl plates): v_{N-H} 3361 cm⁻¹; v_{N-D} 2490 cm⁻¹; see Figure S3. UV/Vis (toluene): λ_{max} 497 nm; ϵ 3700 m⁻¹ cm⁻¹. Elemental analysis was not feasible due to instability. Single crystals suitable for X-ray diffraction were obtained using a similar procedure, quickly combining Et₂O solutions of 1, DBU, and N₂H₄ in a 1:2:2 molar ratio and immediately cooling to -40 °C.

X-ray Crystallography: A crystal was placed onto the tip of a 0.1 mm diameter glass fiber and mounted on a Siemens SMART CCD platform diffractometer for data collection at 193(2) K.^[25] The full data collection was carried out using Mo- K_{α} radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 5.09 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.25° steps in ω at four different ϕ settings and a detector position of -28° in 2θ . The intensity data were corrected for absorption.^[26] Final cell constants were calculated from the xyz centroids of 4012 strong reflections from the actual data collection after integration.^[27]

The two independent iron-diketiminate moieties are related by a pseudo-inversion center located at the midpoint of the iron atoms. The bridging sulfide and hydrazine ligands, however, are not related by the center, nor are there any significant unassigned electron density peaks to suggest disorder. Likewise the cocrystallized DBU molecule does not possess inversion symmetry and no electron density peaks suggested disorder. Initially, space group P1 was selected because the E^2 -1 value was 0.754. Afterwards the Flack parameter refined to 0.227(14), which confirmed the choice of the chiral space group. As

SHORT COMMUNICATION

a further test, the structure was also refined in space group $P\bar{1}$ with the bridging ligands modeled as disordered with each other over a crystallographic inversion center and with the DBU molecule modeled as disordered over another center: the R1 value increased by over 3%. Thus the structure is best represented in chiral space group P1 as an inversion twin with a component mass ratio of 73:27.

Although one cocrystallized pentane solvent molecule was identified and located in the difference Fourier map, it was disordered over multiple positions. Reflection contributions from this solvent molecule were removed using the Squeeze function of program Platon,^[28] which determined there to be 44 electrons in 182 Å³ removed per unit cell. Because the amount and identity of the solvent were known, the solvent was included in the molecular formula. The bridging hydrazine ligand is modeled as disordered over two positions (53:47). Due to the proximity of atom N2' to atom N1 (atoms from different orientations of the hydrazine ligand disorder), the two N–N bond lengths (N1–N2 and N1'–N2') were restrained to be similar. Additionally, the anisotropic displacement parameters for atoms N1 and N2' were constrained to be equivalent. There is one cocrystallized DBU molecule per diiron molecule that is hydrogen-bonded via the hydrazine ligand. A full ORTEP diagram including the DBU is in Figure S4.

Supporting Information (see footnote on the first page of this article): NMR spectra of **3**; details on X-ray crystal structure of **3**•**DBU**.

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