Ammonia Formation by a Thiolate-Bridged Diiron Amide Complex as a Nitrogenase Mimic

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1. Introduction

- Nitrogen fixation has been important subject because it is essential to the input of nitrogen from N_2 into the global biogeochemical N-cycle.

- Haber–Bosch process is a practically-applied method of nitrogen fixation, which consumes much energy for high temperature and pressure.

- In contrast, nitrogenase produces ammonia from dinitrogen at ambient conditions.

- Previous studies, including density functional theory (DFT) calculations, have proposed that transformation by nitrogenase is mediated by two iron atoms in the $[Fe_7MoS_9C]$ core structure, so called FeMo-cofactor, through a series of N_xH_y bridged intermediates (Figure 1).[1]

- In one-iron system, reduction process of nitrogen was studied and two probable mechanism were suggested; distal and alternative mechanism.[2] *However*, there are no report about reduction process in multi-iron system.
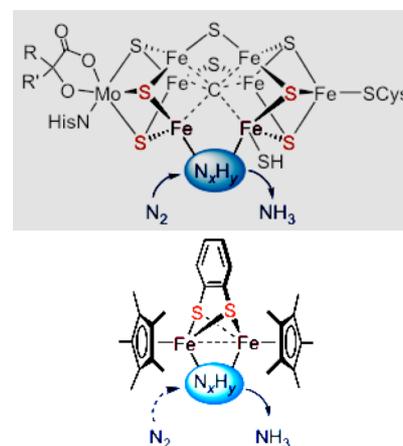
Figure 1. Hypothetical diironsites of ammonia production from dinitrogen. Possible routes are shown for the FeMo-cofactor (upper) and diiron model complex of this work.

In this work, authors synthesized new diiron complex with the bidentate ligand benzene-1,2-dithiolate (bdt), to realize and determine the sequence of protonation and reduction of hydrazine to ammonia.

2. Results and Discussion

2.1. Synthesis, characterization and interconversion of diiron N_xH_y complexes (Scheme 1).

- First the diiron precursor **1** was synthesized in a reported manner using Li_2(bdt).

- bdt ligand: Able to act either as a dianionic (in normal system) or a π-radical monoanionic ligand (in electron-deficient system, C3–C4 and C5–C6 bonds get shorter than other C–C bonds)[3] —> Able to support variable coordination geometries of nitrogen

- Electron deficiency of **1** according to shorter C–C bond —> Good candidate as a nitrogenase model

- Asymmetrical $\mu\text{-}\eta^2\text{:}\eta^4$ structure of bdt

- Next **1** was converted to **2a** by addition of anhydrous hydrazine.

- **2a** has a symmetrical structure according to ^{1}H NMR.

- ^{15}N NMR of ^{15}N-labeled **2a** indicated two equivalent sp^2-hybridized nitrogen atoms.
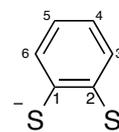
Scheme 1. Synthesis of diiron N_xH_y complexes and their methyl-substituted analogues.
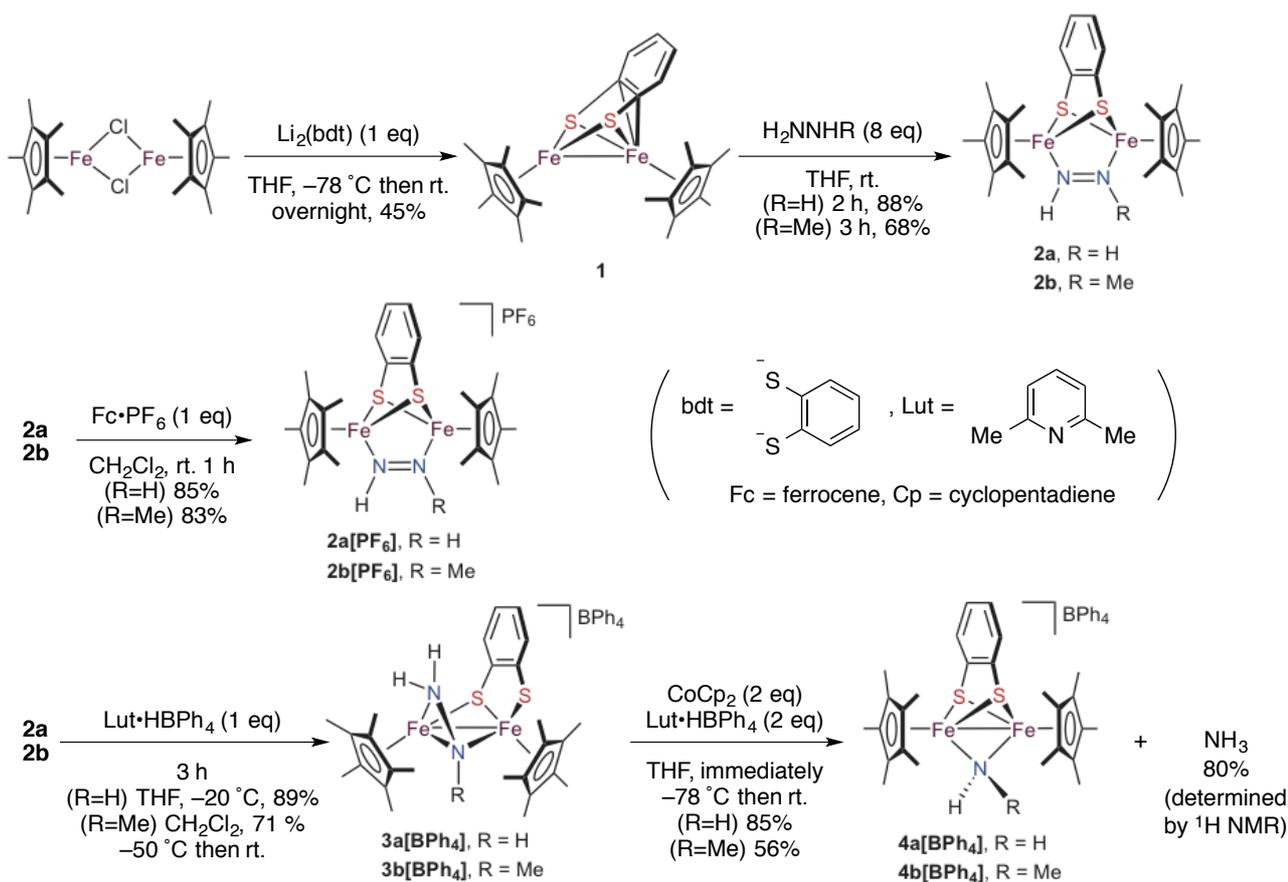
- Due to high air sensitivity and good solubility of **2a**, XRD spectrum of **2a** cannot be taken.
  —> For further analysis, **2a** was oxidized by ferrocenium hexafluorophosphate to afford **2a**[PF$_6$].
- According to XRD analysis of **2a**[PF$_6$] (Figure 2a) …
  ➢ N$_2$H$_2$ ligand coordinating [Fe$_2$S$_2$] scaffold in a *cis* fashion
  ➢ Long Fe···Fe distance (3.176 Å): Absence of bonding interaction
  ➢ N–N distance (1.312 Å): Close to the value of end-on bridging N(sp^2)=N(sp^2) double bond
  ➢ Distance of C–C in bdt: Consistent —> Dianionic bdt ligand
    —> Electron deficiency on diiron center was disappeared.
- Analysis on **2a** and **2a**[PF$_6$] above proved N$_2$H$_2$ ligand is diazene rather than the hydrazido(2-) ligand.

- Then auther couducted protonation-induced reduction on **2a** using Lut•HBAr$_4$ (Ar = Ph or 3,5-bis(trifluoromethyl)phenyl, abbreviated to Ar^F) as a proton source to obtain **3a**[BAr$_4$]
  ➢ Valences of iron atoms rised: Fe^{II}–Fe^{II} (**2a**) —> Fe^{III}–Fe^{III} (**3a**[BAr$_4$])
- Solid state structure of **3a**[BAr$^F_4$] revealed μ-η^1:η^2 N$_2$H$_3^-$ ligand bridging diiron center (Figure 2b).
  ➢ Shorter Fe–Fe distance (2.6990 Å): Existence of bonding interaction
  ➢ Longer N–N bond than that of **2a** (1.402 Å): Single bond
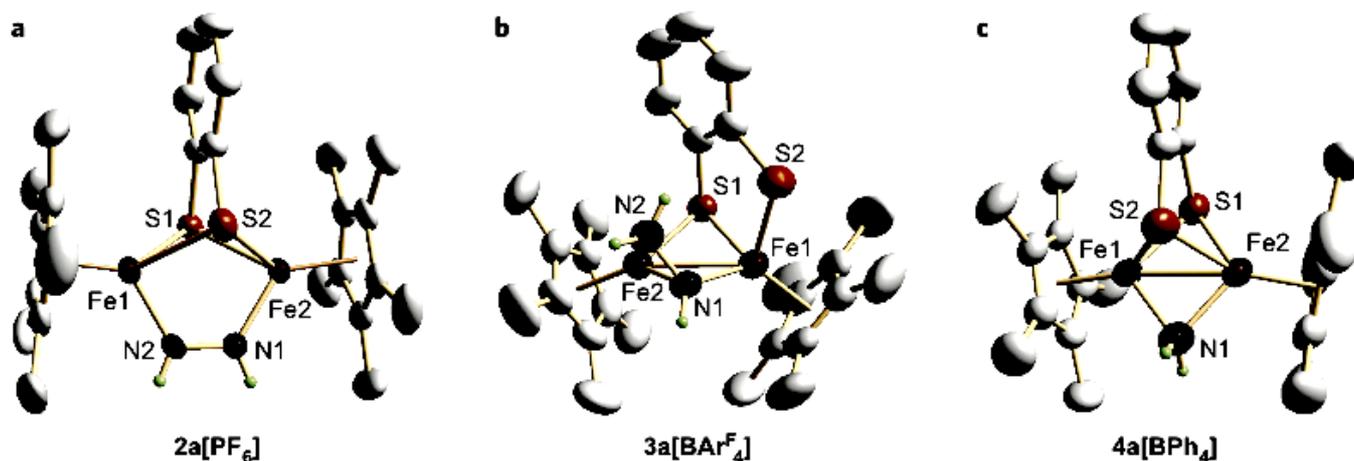
Figure 2. Oak Ridge thermal ellipsoid plot (ORTEP) diagrams, with the thermal ellipsoids shown at a 50% probability level. Anions, one THF molecule and hydrogen atoms on carbons are omitted for clarity.

- ➢ Fe–N distances (Fe2–N1 1.892 Å, Fe1–N1 1.907 Å, Fe2–N2 1.937 Å): sp^3-hybridized N
- · $^{15}N\{^1H\}$ NMR analysis of ^{15}N-labeled **3a**[BPh$_4$] showed two resonances, which split into doublet (111.58 ppm) and triplet (33.05 ppm) without ^1H decoupling. —> Presence of –NH and –NH$_2$

- · Further reduction and protonation of **3a**[BPh$_4$] was conducted using cobaltocene (CoCp2) and Lut•HBPh4 to obtain **4a**[BPh$_4$] with release of NH$_3$ (80%, determined by ^1H NMR).
- · Crystal structure of **4a**[BPh$_4$] showed a bridging NH$_2^-$ ligand binding to thd diiron centers (Figure 2c).
  - ➢ Fe–N distances (1.924 and 1.932 Å): Coordination of sp^3-hybridized nitrogen to iron
  - ➢ Fe–Fe distance (2.4423 Å): Bonding interaction
- · $^{15}N\{^1H\}$ NMR analysis of ^{15}N-labeled **4a**[BPh$_4$] showed one resonance, which split into triplet without ^1H decoupling. —> Presence of NH$_2^-$

2.2. Study of the reaction process from 3a$^+$ to 4a$^+$ by DFT calculation and methylhydrazine experiment

- · DFT model calculation were performed to study the reaction process from **3a**[BPh$_4$] to **4a**[BPh$_4$].
  - ➢ To make calculation simple, Cp* was modelled by Cp (η^5-C$_5$H$_5$).
  - ➢ Cationic part of **3a**[BPh$_4$] —> [CpFe(μ-η^1:η^2-bdt)(μ-η^1:η^2-NH$_2$–NH)FeCp]$^+$ (**3am**$^+$)
    Cationic part of **4a**[BPh$_4$] —> [CpFe(μ-η^2:η^2-bdt)(μ-NH$_2$)FeCp]$^+$ (**4am**$^+$)
- · According to the free energy in solution (Scheme 2),
  - ➢ Cleavage of the N–N bond to liberate NH$_3$ occurs through HN···NH rather than H$_2$N–NH$_2$ moiety.
  - ➢ Ammonia release was mainly derived from the umbridged NH$_2$ of **3am**$^+$.
- · Methylhydrazine experiment supported that ammonia release occurs from unbridging NH$_2$ of N$_2$H$_3^-$ experimentally.

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Scheme 2. Computed minimum free-energy pathway for the transformation of **3am⁺** to **4am⁺**. Relative free energis in solution (ΔG_R) and in the gas phase (in parantheses) are in kcal mol⁻¹.
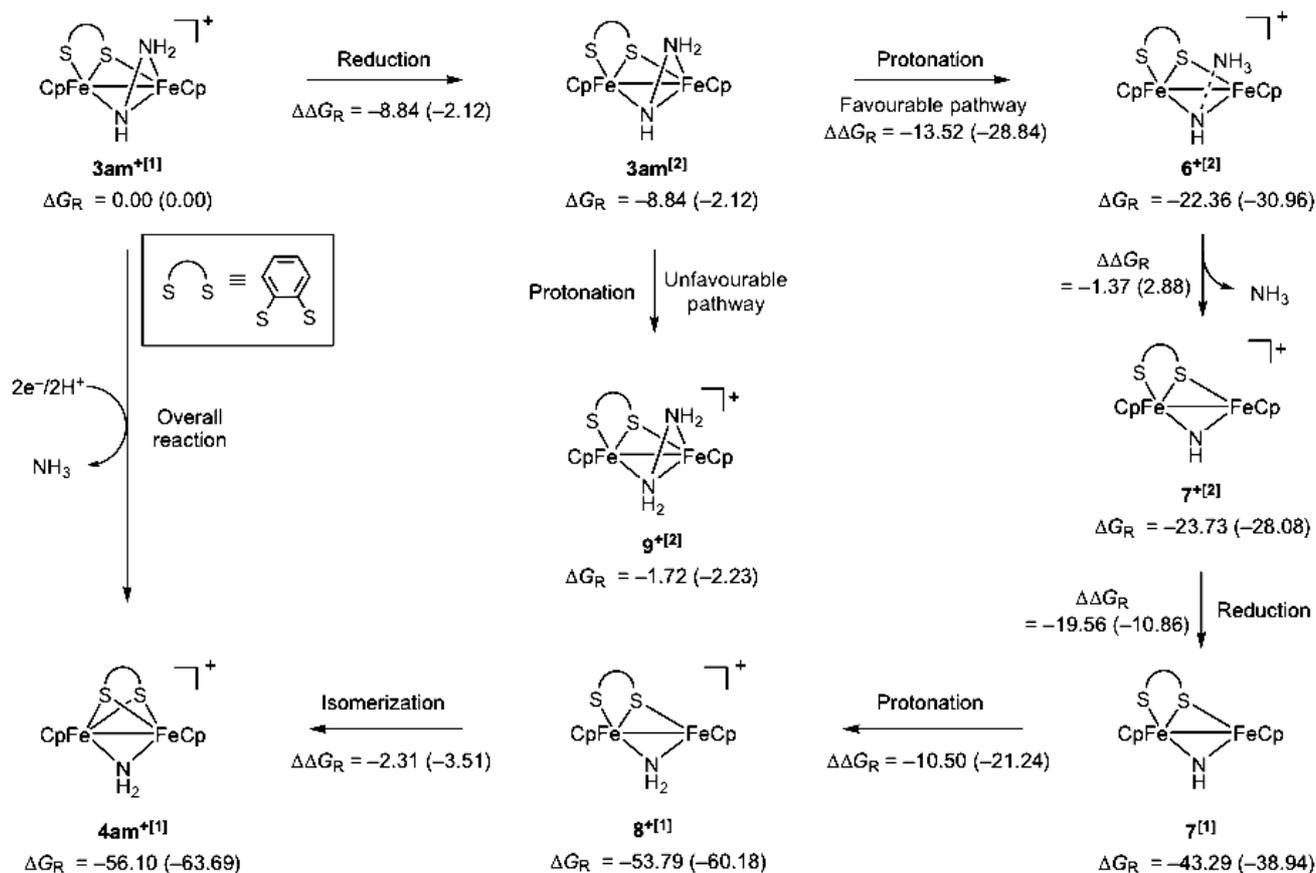
2.3. Ammonia release from complex 4a[Bh₄] in water (Table 1).

- According to Table 1, both water as a weakly acidic proton source (to suppress generation of hydrogen) and strong reductant are crucial for good yield.

3. Conclusion

Authors designed and synthesized a new diiron complex

Table 1. Ammonia production from complex **4a[BPh₄]** in the presence of reducing agent and proton source.

Entry	Reducing agent	$E_{1/2}$ (V)*	Proton source	Yield of NH₃ (%)
1	CoCp₂ (2 eq)	−1.15	Lut·HBPh₄ (2 eq)	46
2	CoCp₂ (6 eq)		Lut·HBPh₄ (6 eq)	51
3	CoCp₂ (2 eq)		H₂O (50 eq)	98
4	CrCp₂ (2 eq)	−0.88	H₂O (50 eq)	8
5	CoCp*₂ (2 eq)	−1.87	H₂O (50 eq)	96
6	CrCp*₂ (2 eq)	−1.35	H₂O (50 eq)	93
7	CoCp₂ (2 eq)		CH₃OH (50 eq)	15
8	None		H₂O (50 eq)	Trace
9	CoCp₂ (2 eq)		None	4

[Cp*Fe(μ-η²:η⁴-bdt)FeCp*] (**1**). Stepwise protonation and reduction of hydrazine to ammonia was realized, which proposed the process of nitrogen fixation.

1 (a) Kaestner, J.; Blochl, P. E. *J. Am. Chem. Soc.* **2007**, *129*, 2998–3006. (b) Dance, I. *Dalton Trans.* **2008**, 5977–5991.
2 (a) Barney, B. M. *et al Proc. Natl. Acad. Sci.* **2006**, *103*, 17113–17118. (b) Hoffman, B. M.; Dean, D. R.; Seefeldt, L. C. *Acc. Chem. Res.* **2009**, *42*, 609–619.
3 Ray, K.; Bill, E.; Weyhermuller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2005**, *127*, 5641–5654.