

A Terminal N₂ Complex of High-Spin Iron(I) in a Weak, Trigonal Ligand Field

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S Supporting Information

ABSTRACT: The role of Fe in biological and industrial N₂ fixation has inspired the intense study of small molecule analogues of Fe-(N_xH_y) intermediates of potential relevance to these processes. Although a number of low-coordinate Fe-(N₂) featuring varying degrees of fidelity to the nitrogenase active site are now known, these complexes frequently feature strongly donating ligands that either enforce low- or intermediate-spin states or result in linear Fe-(N₂)-Fe bridging motifs. Given that the nitrogenase active site uses weak-field sulfide ligands to stabilize its reactive Fe center(s), N₂ binding to high-spin Fe is of great interest. Herein, we report the synthesis and characterization of the first terminal N₂ complex of high-spin (*S* = 3/2) Fe(I) as well as a bridging Fe-(N₂)-Fe analogue. Electron paramagnetic resonance and solution magnetic moment determination confirm the high-spin state, and vibrational experiments indicate a substantial degree of activation of the N≡N bond in these complexes. Density functional theory calculations reveal an electronic structure for the terminal adduct featuring substantial delocalization of unpaired spin onto the N₂ ligand.

The fixation of atmospheric N₂ is an essential process in both the natural world and modern human society.¹ Given the kinetic challenges of activating the N-N triple bond and the inherent chemical complexity of such a process, the systems responsible for biological² and industrial³ N₂ fixation have been subjected to intense scrutiny. Despite recent advances in the field, the detailed mechanism of N₂ fixation by nitrogenase has yet to be fully elucidated.⁴ Indeed, some of the proposed elementary steps of this mechanism are without synthetic precedent. Inspired by the FeMoco active site of nitrogenase (Figure 1B) (and its non-Mo congeners),⁵ the synthetic inorganic community has targeted model complexes to reveal the fundamental chemistry of N₂ activation at transition-metal centers,⁶ culminating in the discovery of synthetic molecular systems based on Mo⁷ and Fe⁸ for the catalytic reduction of N₂ to NH₃.

Although an N₂ adduct of the FeMoco has not yet been characterized, biochemical studies have provided compelling evidence for Fe as the likely site(s) of N₂ binding.⁴ Concurrently, a wealth of model chemistries for N₂ and related nitrogenous substrates have been discovered with Fe-based molecular systems,⁹ including systems capable of facile, reversible N≡N cleavage.¹⁰ Although the coordination chemistry of N₂ with Fe has been studied since the 1970s,¹¹

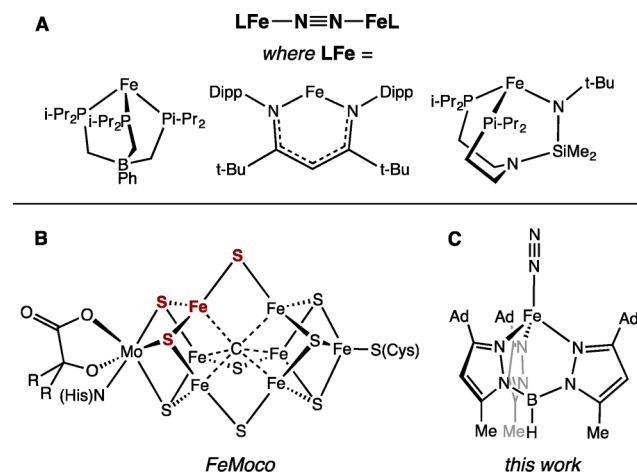


Figure 1. (A) Examples of previously reported Fe-(μ -N₂)-Fe complexes that possess local spin states of *S* > 1. (B) The FeMoco active site of nitrogenase with a potential N₂ binding site highlighted. (C) A terminal N₂ complex of *S* = 3/2 Fe(I) (this work).

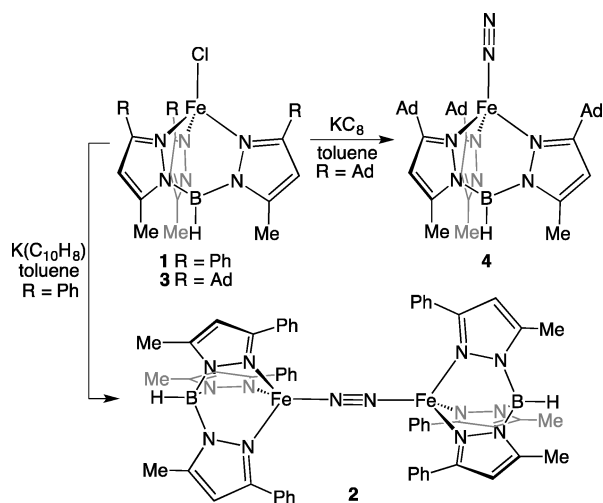
most Fe-(N₂) complexes are diamagnetic, 18-electron species,⁹ and only recently have paramagnetic Fe-(N₂) complexes been fully characterized.¹² Many of these complexes are supported by sterically demanding, strong-field ligands such as phosphines or redox-active pyridine-diimine (PDI) ligands resulting in spin states of *S* = 1/2 or 1 at Fe. These species stand in contrast to a hypothetical N₂ adduct of a belt Fe of FeMoco. Given the weak-field nature of sulfide ligands, such a complex would likely feature a locally high-spin Fe (Figure 1B). Targeting synthetic models of N₂ coordination to high-spin Fe in weak ligand fields is therefore an important area of study. The only Fe-(N₂) complexes thought to have local spin states greater than *S* = 1 are linear Fe-(μ -N₂)-Fe bimetallic complexes supported by β -diketimate (NacNac),^{12a} tris(phosphinomethyl)borate (PhBP^{iPr}₃),^{12b} or hybrid phosphine/amide^{12c} ligands (Figure 1A). The bimetallic nature of these complexes complicates the analysis of the local ligand field and spin state at Fe, and while these complexes are capable of substantial N₂ activation, the bridging N₂ ligand does not experience the polarization of both spin and electron density expected for a terminal N₂ adduct. Prior to this work, terminal high-spin Fe(I)-(N₂) complexes had not been isolated. Herein, we report the synthesis and characterization of such a complex along with its bridging analogue.

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With sufficiently bulky substituents at the 3-position of the pyrazole rings, four-coordinate TpFe complexes can be isolated.¹³ Of these complexes, (PhTp^{ibu})Fe(CO) prepared by Parkin et al. is the lone example of a monovalent TpFe complex.¹⁴ We were curious to ascertain if an analogous N₂ complex could be prepared and if such a complex might adopt a high-spin state. To wit, reduction of the known complex Tp^{Ph,Me}FeCl¹⁵ (**1**) with potassium naphthalenide in toluene gave the deep burgundy N₂-bridged dimer (Tp^{Ph,Me}Fe)₂(N₂) (**2**, Scheme 1). Single-crystal X-ray diffraction (XRD)

Scheme 1



performed on **2** reveals a staggered orientation of the two Tp ligands with an essentially linear Fe–(N₂)–Fe linkage ($\angle\text{Fe}–\text{N}–\text{N} = 177.7^\circ$) which sits on a crystallographically imposed inversion center (Figure 2). The N–N bond length of 1.1804(19) Å for **2** is similar to that found in [(NacNac)Fe]₂(N₂) complexes and indicative of substantial backbonding from the Fe centers.

The IR spectrum of **2** is featureless in the region containing N–N stretching bands; however, Raman spectroscopy reveals

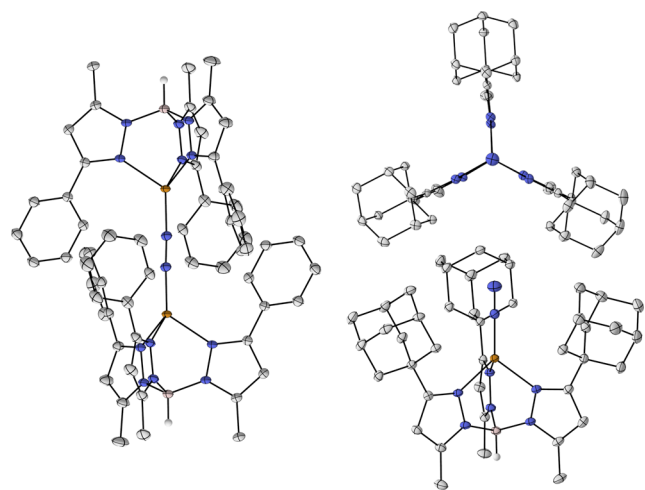


Figure 2. Thermal ellipsoid plots (50% probability) of the solid-state structures of **2** (left) and **4** (top view, top right; side view, bottom right). Orange, blue, pink, and gray ellipsoids represent Fe, N, B, and C atoms, respectively. Hydrogen atoms bonded to carbon and cocrystallized solvent molecules are omitted for clarity.

an absorption at 1779 cm⁻¹, consistent with a strongly activated N₂ unit. Solution magnetic moment determination by the method of Evans gives a value for μ_{eff} of $6.9 \pm 0.2 \mu_{\text{B}}$, consistent with a well-isolated $S = 3$ ground state at ambient temperature (spin-only value for $S = 3: 6.9 \mu_{\text{B}}$). Either strong ferromagnetic superexchange coupling between two $S = 3/2$ Fe(I) centers or a three-spin ferrimagnetic interaction involving two $S = 2$ Fe(II) centers coupled antiferromagnetically to a triplet (N₂)²⁻ ligand would be consistent with these data. However, ferromagnetic superexchange coupling via N₂ is typically weak,¹⁶ at odds with the effective magnetic moment observed for **2** at ambient temperature. The latter three-spin model has been used to explain magnetic Mossbauer data collected on the related [(NacNac)Fe]₂(μ -N₂).¹⁷ Given its similarity to these complexes, the three-spin model is a compelling description for **2**. This analogy is further supported by the presence of an intense near IR band (903 nm, 3300 M⁻¹cm⁻¹) observed for **2** (see Supporting Information, SI) similar to that observed in the neutral [(NacNac)Fe]₂(μ -N₂) complexes.¹⁸ Detailed spectroscopic and magnetic studies are underway to further characterize these interactions.

The successful synthesis of **2** led us to explore the possibility of stabilizing an analogous terminal Fe–(N₂) complex through the introduction of vertically oriented steric bulk at the 3-position of the pyrazole donors. We therefore prepared the complex Tp^{Ad,Me}FeCl (**3**) that was then reduced by KC₈ in toluene to give pale purple Tp^{Ad,Me}Fe(N₂) (**4**) (Scheme 1). XRD on single crystals of **4** grown from toluene reveals an approximately three-fold symmetric pseudotetrahedral coordination sphere at Fe,¹⁹ with a N≡N distance of 1.1187(17) Å (Figure 2). In contrast to **2**, solid samples of **4** possess an intense IR absorption at 1959 cm⁻¹, consistent with a strongly activated, terminally bound N₂ ligand. Evans' method data on **4** give a value for μ_{eff} of $3.8 \pm 0.2 \mu_{\text{B}}$, consistent with an $S = 3/2$ Fe(I) center. The most compelling evidence for the assignment of a high-spin state for **4** comes from X-band EPR spectroscopy. A frozen toluene solution of **4** at 106 K reveals prominent features at $g_{\text{eff}} = 4.0$ and $g_{\text{eff}} = 2.0$ consistent with transitions within the $m_s \pm 1/2$ doublet of an axial $S = 3/2$ system (Figure 3).²⁰ Under the conditions investigated, no hyperfine structure was resolved.

Density functional theory (DFT) calculations (M06L²¹ with a custom Alrichs²² basis set via ORCA,²³ see SI) were carried out on the model complex TpFe(N₂) in order to gain insight into the electronic structure of **4**. Geometry optimization on the quartet surface reproduced the experimental geometry well, yielding an essentially C_{3v} structure in the absence of any symmetry constraints. Optimization on the doublet surface resulted in a higher energy structure (by $\sim 0.035 E_{\text{h}}$) that deviated substantially from three-fold symmetry, lending further support for an $S = 3/2$ assignment for **4** (see SI). Interestingly, Mulliken spin population analysis designates only two atoms in the molecule with significant spin density (>0.05): Fe (3.31) and the distal nitrogen of the N₂ ligand (N _{β} , -0.24) (Figure 4).

The one-electron frontier molecular orbitals calculated for TpFe(N₂) provide some insight into the origin of this spin distribution (Figure 5). While care should be taken in the interpretation of canonical orbitals,²⁴ the orbital structure shown in Figure 5 is not readily described in terms of five, two-electron d-orbitals that are filled according to the Aufbau principle in either a low- or high-spin configuration. The lowest-energy d-orbital has d_{z²} parentage followed by a

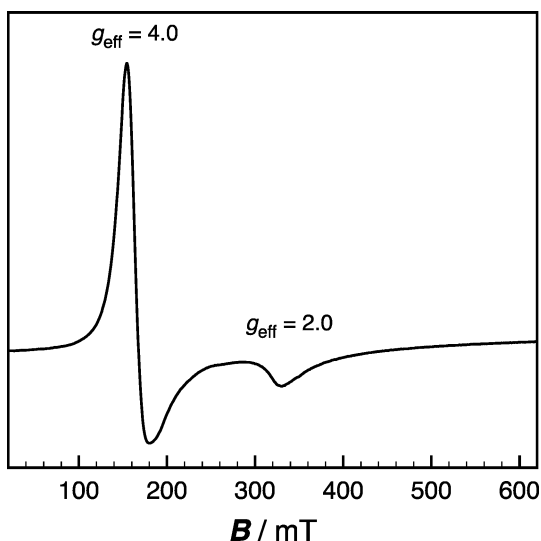


Figure 3. X-band EPR spectrum of **4** at 106 K in a toluene glass collected at a microwave frequency of 9.326 GHz.

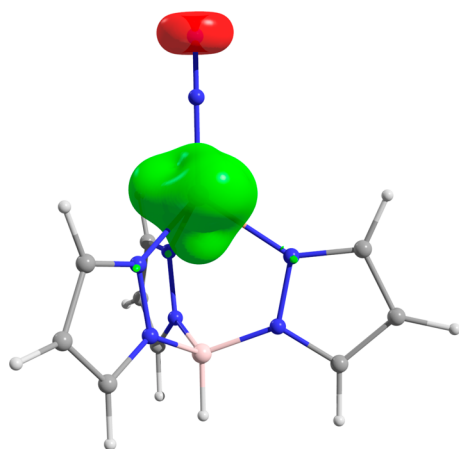


Figure 4. Spin-density isosurface calculated for the model complex $\text{TpFe}(\text{N}_2)$. Green represents positive spin and red represents negative spin. Mulliken spin populations: $\text{Fe} = 3.31$, $\text{N}_\beta = -0.24$.

degenerate set that is essentially nonbonding with respect to the σ -bonding framework of the molecule. A second e set higher in energy is antibonding with respect to the Tp-Fe σ -bonds with some delocalization on to the N_2 ligand. The remaining two β -spin electrons reside in a pair of approximately degenerate orbitals that exhibit substantial backbonding to the N_2 ligand. The spin density found on the distal nitrogen of the bound N_2 ligand is presumably a result of this differential backbonding in the α - and β -spin manifolds. One interpretation of these results would place **4** on a continuum in between $\text{Fe}(\text{I})-(\text{N}_2)$ and $\text{Fe}(\text{III})-(\text{N}_2)^{2-}$, by analogy to the N_2 -bridged diiron complex **2** and related complexes,²⁵ although the latter formulation would admittedly be extreme. More detailed computational study of these complexes will accompany further spectroscopic investigations.

In summary, through the use of a bulky Tp supporting ligand, we have synthesized the first example of a terminal N_2 complex of high-spin $\text{Fe}(\text{I})$. EPR studies unequivocally indicate an $S = 3/2$ ground state for **4**. This assignment is further substantiated by magnetic moment determination and DFT calculations, the latter of which indicate substantial spin

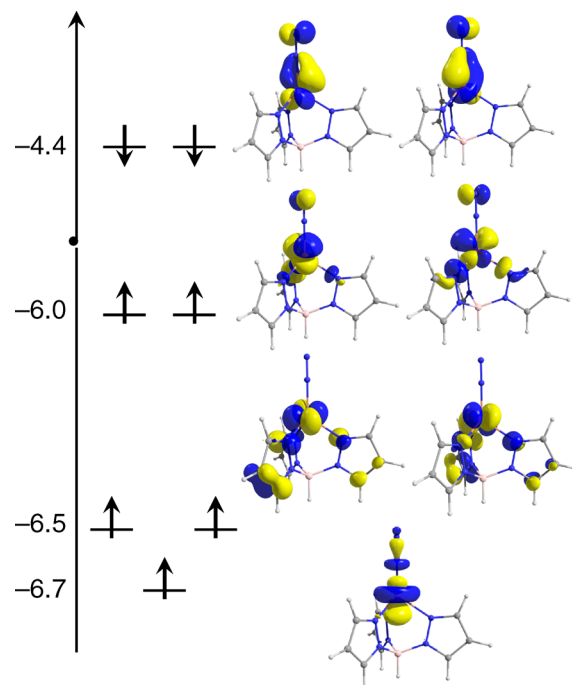


Figure 5. Canonical single-electron Kohn–Sham orbitals calculated for $\text{TpFe}(\text{N}_2)$ (see text for computational details). Orbital energies are in eV.

polarization of the N_2 ligand. This work definitively establishes the viability of terminal N_2 coordination to high-spin $\text{Fe}(\text{I})$, and the weak-field nature of **4** renders it a compelling model for hypothetical N_2 binding in a terminal mode to an unsaturated Fe site in nitrogenase. Future studies are directed toward spectroscopic corroboration of the spin-polarization of the N_2 ligand of **4** and the potential ramifications of this electronic structure on subsequent N_2 functionalization reactivity.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures and characterization, spectroscopic data, crystallographic analyses, and computational data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06337.

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Notes

The authors declare no competing financial interest.

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