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Isolation and Characterization of a High-Spin Mixed-Valent Iron Dinitrogen Complex

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Dedicated to Richard A. Andersen, an amazing scholar and mentor, on the occasion of his 75th birthday.

We report a rare example of a mixed-valence iron compound with an FeNNFe core, which gives insight into the structural, spectroscopic, and magnetic influences of single-electron reductions and oxidations. In the new compound, the odd electron is localized as judged from Mössbauer spectra at 80 K and infrared spectra at room temperature, and the backbonding into the N₂ unit is intermediate between diiron(I) and diiron(0) congeners. Magnetic susceptibility and relaxation studies on the series of FeNNFe compounds show significant magnetic anisotropy, but through-barrier pathways enable fairly rapid magnetic relaxation.

Both natural and industrial nitrogen fixation use catalysts with multiple iron atoms in their active sites. In nature, nitrogenase enzymes employ mixed-valence FeS clusters to carry out the reduction of N₂ with protons and reducing agents under ambient conditions.1,2,3 Industrial nitrogen fixation uses the Haber-Bosch process to combine N₂ with H₂, and the most common catalyst contains reduced iron that is formed in situ from iron oxide doped with potassium and aluminium.4 The iron atoms in the resulting promoted catalyst have an average oxidation state between 0 and +1.4 We aim to prepare well-characterized small molecules that capture the key properties, such as mixed iron oxidation states and N₂ binding.

To date, only a few examples of bridging Fe-N₂-Fe complexes in mixed-valent states have been characterized.5 The first example was the complex [Fe(N₂)-FeL]2 (L = PhB(CH₂PPh₂)₃) reported by Peters et al., but the valence localization was not established.5 Field and coworkers reported a second example, the mixed-valent iron(II)iron(0) complex [FeH(P( (CH₂)₂P(CH₃)₂)₃)](μ-N₂)(μ-μ-N₂)(μ-μ-μ-P(CH₃)₂P(CH₂)₂)), which features an asymmetric ligand environment.5b On the basis of 1H and 31P spectroscopy, it was assigned as Robin-Day Class I where the oxidation states are completely localized.5b Herein, we report the synthesis of a bimetallic, mixed-valent iron-N₂ complex using a bulkier diketiminate L Me = 2,4-bis(2,6-diisopropylphenylimino)-pent-3-yl and show that the valence is localized using Mössbauer and infrared spectroscopies.

Addition of 1 equiv of potassium graphite (KC₈) to a purple solution of L⁵⁵FeNNFe⁵⁶ (1) and 18-crown-6 (18-c-6) in tetrahydrofuran (THF) resulted in a green mixture. Filtration of this solution through Celite® and vapor diffusion of pentane into the filtrate at -40 °C led to the formation of green crystals of the known analogues 1, [K(18-c-6)(THF)]²[L⁵⁵Fe(μ-μ-N₂)FeLMe][K(18-c-6)(THF)]² (shown in Figure 2) in 63% yield.7 X-ray crystallography of 2 revealed a structure with an N–N distance of 1.186(6) Å, which is significantly longer than that in free N₂ (1.09 Å), suggestive of substantial dinitrogen activation (see Figures 1 and 3).

A comparison of the core bond distances and angles for 2 to those of the known analogues 1, [K(18-c-6)(12-c-4)]²[L⁵⁵Fe(μ-μ-N₂)FeLMe]³ (shown in Figure 2) reveals that the metrical parameters for all four complexes are statistically indistinguishable (Table 1).7

![Figure 1. Synthesis of [L⁵⁵Fe(μ-N₂)FeLMe][K(18-c-6)(THF)]² (2) from the reduction of 1 using KC₈ with 18-crown-6.](image-url)
The fact that the N–N stretching mode is observed in the infrared spectrum indicates that the molecule is not centrosymmetric, despite the inversion center in the X-ray crystal structure. In the previously characterized free N₂ (Figures S-6 and S-7). This 59 cm⁻¹ shift matches well with the elongation of the N–N bond.

### Table 1. Comparison of structural and spectral parameters for complexes 1–4.

| Complex | Formal Ox. State | N–N dist. (Å) | Fe–N₂ dist. (Å) | ν₅–N [ν₂(N₂–NN)](cm⁻¹) | δ (mm s⁻¹) | |δE₀| (mm s⁻¹) |
|---------|----------------|--------------|-----------------|------------------------|-----------|-----------|
| 1       | Fe⁺Fe⁻       | 1.186(7)     | 1.745(3)        | 1810 [1745]            | 0.62⁶     | 1.41³     |
| 2       | Fe⁻Fe⁺       | 1.186(6)     | 1.744(3)        | 1749 [1690]            | 0.63      | 1.75      |
| 3       | Fe⁺Fe⁻       | 1.190(8)     | 1.758(4)        | 1683 [1632]            | 0.45      | 1.74      |
| 4       | Fe⁺Fe⁺       | 1.215(6)     | 1.750(4), 1.755(5) | 1625[1566]            | 0.47      | 2.48      |

⁶Values obtained from resonance Raman spectroscopy in refs 7a and 7b. From Mössbauer spectra of solid 4.2 K from ref 12. From Mössbauer spectra of solid at 170 K from ref 12.

The zero-field Mössbauer spectrum of 2 (Figure 4) is best fit with two overlapping quadrupole doublets of identical intensity. A staggered fit yielded parameters δ₁ = 0.48 mm s⁻¹ and |ΔE₀|₁ = 1.71 mm s⁻¹ and δ₁ = 0.62 mm s⁻¹ and |ΔE₀|₂ = 1.75 mm s⁻¹ for the two components (Figure 4; alternate fits shown in Figures S-2 and S-3). The isomer shift for component 1 (δ₁) is similar to that in the diiron(I) analogue 1, and δ₂ is similar to that in the diiron(0) analogues 3 and 4, supporting the localization of distinct iron(I) and iron(0) sites in 2 (Table 1). An alternative nested fit (Figure S-2) has very similar isomer shift parameters. The sequential one-electron reductions of the core from 1 to 2 and 2 to 3 lead to bathochromic shifts of the N₂ stretch by 61 cm⁻¹ and 66 cm⁻¹ respectively. The red-shifting of the N–N bond.

Interestingly, complexes 1, 2, and 3 are congeners that span three oxidation states of the diiron core — FeFe⁺, FeFe⁻ and Fe⁺Fe⁺ — with no other differences in the primary coordination environment. The sequential one-electron reductions of the core from 1 to 2 and 2 to 3 lead to bathochromic shifts of the N₂ stretch by 61 cm⁻¹ and 66 cm⁻¹ respectively. The red-shifting of the N–N bond.

In the IR spectrum of 2, there is a weak band at 1749 cm⁻¹, which shifts to 1690 cm⁻¹ when 2 is synthesized under ¹⁵N₂ (Figures S-5 and S-7). This 59 cm⁻¹ shift matches well with the 61 cm⁻¹ shift predicted using a harmonic oscillator model. The ν₅–N peak for 2 is significantly red-shifted compared to that of free N₂ (ν₀–N = 2359 cm⁻¹),⁵ consistent with the N–N bond elongation in 2 as characterized by X-ray diffraction, demonstrating substantial reduction of the bound dinitrogen unit. The fact that the N–N stretching mode is observed in the infrared spectrum indicates that the molecule is not centrosymmetric, despite the inversion center in the X-ray crystal structure. In the previously characterized 1, 3, and 4 (as well as alkali-substituted congeners of 4, analogues with larger β-diketiminate ligands, and Co and Ni analogues), the N–N stretching vibrations were infrared silent and thus were measured using resonance Raman spectroscopy.⁷ To our knowledge, the only IR-observable N–N vibrations in dinuclear β-diketiminate-supported MNMN systems have been in compounds with asymmetric cores: a spectroscopically characterized FeNNCo species⁸ and a NiNNNi species with an asymmetrically coordinated potassium cation.¹⁰

Interestingly, complexes 1, 2, and 3 are congeners that span three oxidation states of the diiron core — FeFe⁺, FeFe⁻ and Fe⁺Fe⁺ — with no other differences in the primary coordination environment. The sequential one-electron reductions of the core from 1 to 2 and 2 to 3 lead to bathochromic shifts of the N₂ stretch by 61 cm⁻¹ and 66 cm⁻¹ respectively. The red-shifting of the N–N stretch results from the population of orbitals that backbond into the π* orbitals of the N₂ unit, decreasing the bond order of the N–N bond. The series 1-3 is distinctive, because the influence of the metal oxidation states can be discerned without coordinated alkali metal cations. This is important because alkali metal cations⁹ and other Lewis acids can further weaken the N–N bond.
values but different quadrupole splitting, which would not make sense for a delocalized system. Given the similarity of the Mössbauer parameters to very similar diiron(0) and diiron(I) analogues, it is most reasonable to use the staggered fit.

As described above, the previously reported mixed-valent Fe–N2–Fe complexes were assigned as either Robin-Day Class I mixed-valent with full localization\(^5b\) or Robin-Day Class III with full delocalization down to 80 K.\(^5b,c\) For \(2\), the presence of an N2 stretching vibration in the IR spectrum and two doublets in the Mössbauer spectrum together indicate localization of the additional electron on one of the two iron sites. However, the room temperature \(^1\)H NMR spectrum of \(2\) collected in THF-\(d_8\) exhibits \(8\) resonances, with integrations that are most consistent with \(D_2d\) or \(D_2h\) symmetry (Figures S-4 and S-5). Therefore, the electron can sample both of the iron sites on the NMR timescale in solution. This is most consistent with Robin-Day Class II mixed valency, though there may be structural differences in solution (see below).\(^6\)

Figure 4. Zero-field Mössbauer spectrum of solid \(2\) at 80 K. Fitting to one doublet gave poorer agreement (Figure S-3).

Using the Evans method, the room-temperature solution magnetic moment of \(2\) in THF was \(\mu_{\text{eff}} = 6.6 \mu_B\). Solid-state magnetic susceptibility data were also collected using a SQUID magnetometer, and above 50 K, the molar magnetic susceptibility times temperature \((\chi M T)\) for \(2\) collected under applied fields of 0.1 - 7 T each approach \(7 \text{ cm}^3 \text{ K mol}^{-1}\) above 50 K (Figure S-11), consistent with an overall \(S = 5/2\) ground state. A sextet ground state can be rationalized either with ferromagnetic coupling between high-spin iron(I) \((S = 3/2)\) and high-spin iron(0) \((S = 1)\), or with a Fe\(^{II}\)-N\(^2\)-Fe\(^{II}\) three-spin model where high-spin iron(II) and iron(II) sites are spin-aligned \((S_{\text{tot}} = 7/2)\) and antiferromagnetically coupled to a triplet N\(^2\)-bridge \((S_{\text{N2}} = 1)\) to give a total \(S = 5/2\) ground state.\(^7,12\) The latter model is more compatible with previous computations on compound \(1\), which predicted an Fe\(^{II}\)-N\(^2\)-Fe\(^{II}\) core with two high-spin iron(II) sites that are antiferromagnetically coupled to a triplet N\(^2\)-bridge to give a \(S = 3\) ground state.\(^7,12\) These three-coordinate iron(II) sites are known\(^12,13\) to have large negative zero-field splitting parameters \((D)\) that suggest the potential for slow magnetic relaxation.\(^14\) Accordingly, we sought to further evaluate the magnetization behaviour of the N\(^2\)-bridged compounds.

The solid-state \(\chi M T\) values of \(1\), \(2\), and \(4\) at room temperature correspond to \(S = 3, 5/2, \) and \(2\) systems, having isotropic \(g\) values of 2.38, 2.60, and 2.28. These spin states agree with solution magnetic moments,\(^7,9\) and the elevated \(g\) values suggest significant spin-orbit coupling. Low temperature magnetization data for \(1\) and \(2\) were collected to examine the magnetic anisotropy and the data were fit to a phenomenological zero-field splitting Hamiltonian. The data for \(1\) could be fit well with multiple sets of parameters and all fits suggested significant axial anisotropy \((D = -45 \text{ cm}^{-1}\) from the best fit) as well as significant transverse anisotropy \((|E/D| = 0.24\) from the best fit). The fit for \(2\) suggested significantly less axial anisotropy \((D = -4.5 \text{ cm}^{-1})\), again with a substantial contribution from transverse anisotropy \((|E/D| = 0.29\) ). In contrast, X-band EPR spectra collected from a frozen 50:1 mixture of THF/2-methylTHF at 4.2 K exhibit several signals from \(S = 5/2\) states.
with positive $D, D > > h\nu$ (microwave quantum), with the majority form having $E/D = 0.097$ (Figure S-24). This difference in the sign of $D$ from the solid-state susceptibility measurements indicates a change in the electronic structure in frozen solution, possibly caused by interactions with the solvent.

Given the evidence of magnetic anisotropy in both 1 and 2 from the dc susceptibility measurements, we collected ac magnetic susceptibility data to probe for slow magnetic relaxation. For 1, 2, and 4, non-zero signal was observed in the out-of-phase magnetic susceptibility ($\chi''$) at the highest frequencies. However, in each case a small bias field was required to see fully resolved peaks within the measured frequency range of 1–1500 Hz (see Figure S for the data for 1 and 2), consistent with systems having both axial and transverse anisotropy. Temperature-dependent magnetic relaxation times ($\tau$) were extracted for 1 and 2 from Cole-Cole fits to the in- and out-of-phase magnetic susceptibility data (the peaks for 4 were too broad for further analysis). Plots of the natural log of $\tau$ versus temperature for 1 and 2 are shown in Figures S-14 and S-18, respectively, and the pronounced curvature in both sets of data indicate that thermally-activated Orbach relaxation is not dominant over the entire measured temperature and frequency range. However, a linear fit to the high temperature data gives lower limits for the spin-reversal barriers, $U_{\text{eff}}$, and upper limits for the attempt times, $\tau_0$. For 1 these limits are $U_{\text{eff}} \geq 6.6 \text{ cm}^{-1}$ and $\tau_0 \leq 6.8 \times 10^{-6} \text{ s}$, and for 2 they are $U_{\text{eff}} \geq 27 \text{ cm}^{-1}$ and $\tau_0 \leq 3.6 \times 10^{-2} \text{ s}$. Thus, although both of these multinuclear systems exhibit significant magnetic anisotropy, their relaxation behavior is very similar to typical mononuclear single-molecule magnets, in that both sets of complexes are strongly affected by through-barrier pathways.

In conclusion, we have described the preparation and characterization of the mixed-valent diiron compound $[\{K(18-c-6)(THF)\}_2\{\mu\text{-N}_2\text{Fe}L\text{Fe}L\}]$, which contains a rare example of an $\text{N}_2$-bridged complex that can be analyzed in several oxidation levels that vary by one electron.\textsuperscript{15} Probing the electronic structure and magnetism in greater detail will be the basis for interesting future studies.

**Conflicts of interest**

There are no conflicts to declare.

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The crystal structure of 2 has been deposited with the CCDC with accession code 1866500.

**Notes and references**


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