

Transformation of an $[\text{Fe}(\eta^2\text{-N}_2\text{H}_3)]^+$ Species to π -Delocalized $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+/1+}$ Complexes

Owing to its biological and industrial relevance, establishing viable mechanisms for N_2 reduction to NH_3 is a longstanding goal of chemists. Several mechanisms have been proposed for a metal-mediated reduction, with the distal (i.e., $\text{M}^n\text{-N}\equiv\text{N} \rightarrow \text{M}^{n+3}\equiv\text{N} + \text{NH}_3 \rightarrow \text{M}^n + \text{NH}_3$) and alternating (i.e., $\text{M}^n\text{-N}\equiv\text{N} \rightarrow \text{M}^n\text{-HN}=\text{NH} \rightarrow \text{M}^n\text{-H}_2\text{N-NH}_2 \rightarrow \text{M}^n + 2 \text{NH}_3$) mechanisms representing the two limiting schemes.¹ Thus, establishing the reactivity patterns and spectroscopic signatures of complexes of the type $\text{M}_x\text{-N}_y\text{H}_z$ ($x \geq 1$, $y = 1\text{-}2$, $z = 0\text{-}6$) is an active area of research.

Due to the inherent instability of diazene, examples of diazene-coordinated metal centers ($\text{M}_x\text{-N}_2\text{H}_2$) remain relatively rare. By using a tris(phosphino)borate ligand scaffold, we have prepared and characterized a pair of diazene-bridged diiron species, $\{[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]\text{Fe}(\text{CO})\}_2(\mu\text{-}\eta^1:\eta^1\text{-N}_2\text{H}_2)^{0/-}$ ($[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+/1+}$); the system is unique in that the congeners differ by one electron, and thus two oxidation states for a $\text{M}_x\text{-N}_2\text{H}_2$ species can be accessed.

The solid-state structures of $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$ and the one-electron reduced congener, $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{1+}$ have been obtained. Crystals of $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{1+}$ suffered from severe solvent disorder, which combined with their small size and extreme oxygen sensitivity, rendered them not suitable for “standard” small molecule Mo- or Cu-tube based diffractometers. Thus, the data for $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{1+}$ was obtained at SSRL Beam Line 12-2.

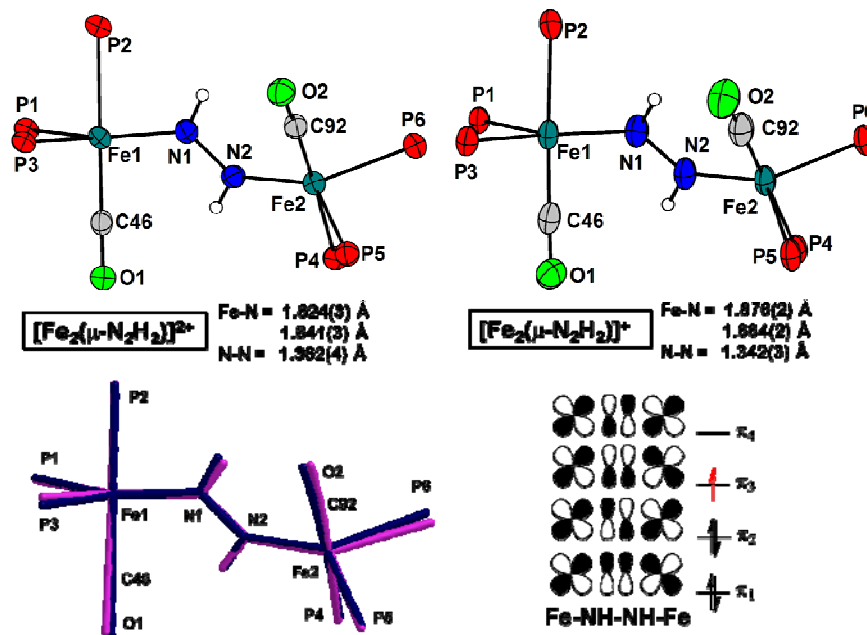


Figure 1. (Top) Thermal ellipsoid (50 %) representation of the core atoms of $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$ (left) and $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{1+}$ (right). (Bottom left) Overlay of the core atoms of the core atoms of $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$ (blue) and $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{1+}$ (purple). (Bottom right) Qualitative MO diagram of the Fe-NH-NH-Fe bond; the π_1 and π_2 levels are filled for $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$; the π_3 orbital is singly occupied in $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{1+}$ (red).

The overall geometry about the two iron centers are similar in both $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$ and $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{1+}$, as shown by the overlay of the core atoms in Figure 1, though discrepancies about the metrical parameters of the Fe-NH-NH-Fe core are present. Upon reduction, the average Fe-N distance *increases* by *ca.* 0.05 Å to 1.88 Å, and the N-N distance *decreases* by *ca.* 0.02 Å.

This structural data, combined with theoretical and spectroscopic data, suggests an unusual electronic structure for $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$. Whereas previously reported M-NH-NH-M complexes of late transition metals feature a 4-center, 6-electron bond π -delocalized bond across the core,² $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$ only has 4 π -electrons in the 4-centered bond (Figure 1). Such an electronic structure has been observed high-valent, early transition metal M-NH-NH-M complexes,³ but is unprecedented in later metals. The different electronic structure observed in $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$ is due to a different geometry about the iron centers. In the 5-coordinate trigonal bipyramidal geometry of $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^{2+}$, each iron center has one d-electron of suitable symmetry to contribute to the bond.

In sum, we have prepared and characterized diazene bridged diiron complexes that are distinct from previously characterized diiron complexes in that they feature fewer π -electrons. The different electronic structure manifests itself in both the structural and spectroscopic features of the complexes. To our knowledge, the mixed-valence species $[\text{Fe}_2(\mu\text{-N}_2\text{H}_2)]^+$ is the first example of a paramagnetic diazene-ligated metal species, and has been characterized by EPR/ENDOR spectroscopy. Whether such a fragment arises in the reaction pathway by which nitrogenase reduces N_2 to 2 NH_3 is now being explored by detailed comparisons of the results presented here with ENDOR results for nitrogenase intermediates.

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(1) (a) Hoffman, B. M.; Dean, D. R.; Seefeldt, L. C., *Acc. Chem. Res.* **2009**, *42*, 609; (b) Chatt, J.; Pearman, A. J.; Richards, R. L., *Journal Of The Chemical Society-Dalton Transactions* **1977**, 1852; (c) Dilworth, M. J.; Thorneley, R. N., *Biochem. J.* **1981**, *193*, 971.

(2) (a) Sellmann, D.; Sutter, J., *Acc. Chem. Res.* 1997, *30*, 460; (b) Lehnert, N.; Wiesler, B. E.; Tuczek, F.; Hennige, A.; Sellmann, D., *J. Am. Chem. Soc.* **1997**, *119*, 8869.

(3) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J., *J. Am. Chem. Soc.* **2005**, *127*, 7901.

Contacts

Caroline Saouma (csaouma@uw.edu) and Jonas Peters (jonas.peters@gmail.com)

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