A Multi-Metallic Iron-Dinitrogen Complex, What is its Electronic Structure?

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Introduction

The Haber-Bosch process for converting N_2 and H_2 into ammonia (NH_3, ~10^8 tons per year) is an integral component of food production, accounting for approximately 50% of the nitrogen in our bodies and consuming greater than 1% of the World's total energy output.[1] While the nitrogenase enzymes can perform this transformation under more mild conditions, there has only been limited success in developing synthetic molecular catalysts.[2]

We are interested in the use of multiple Fe centers acting cooperatively in order to facilitate the conversion of N_2 to NH_3. In the extreme case of complete scission of the N≡N bond, Holland and coworkers have demonstrated that multiple low-coordinate Fe centers can be used to form NH_3 stoichiometrically.[3] However, in the intermediate cases where the N-N bond remains partially intact, the electronic structure of both the metal centers and the N_2 fragment are not necessarily well-defined.[4] For example, while the neutral N_2 molecule is diamagnetic, a putative N_2^{2-} fragment has an S=1 ground state which can interact with paramagnetic metals.

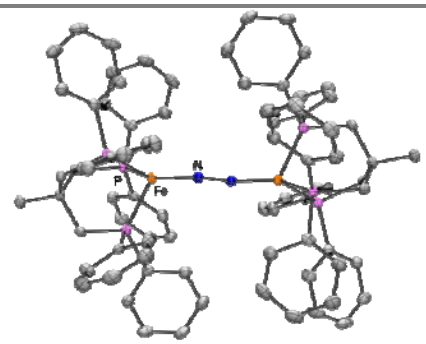

Figure 1: X-ray structure of (Triphos)Fe-N_2-Fe(Triphos) with H atoms omitted.

Experimental

Pulsed-field and DC magnetization measurements were obtained at the Pulsed Field Facility of the NHMFL located at LANL in the 65 T magnet with an extraction magnetometer, and in a 14 T PPMS with a VSM.

Results and Discussion

The "three-spin" model of N_2 reduction proposed by Holland for their formally Fe(I)-N_2-Fe(I) complex involves interpreting it as Fe(II)-(N_2^{2-})-Fe(II) with ferromagnetically coupled Fe centers anti-ferromagnetically coupled to N_2^{2-} (high spin Fe centers). Applying this model to (Triphos)Fe-N_2-Fe(Triphos) (Figure 1), a formally Fe(0) complex would suggest interpretation as Fe(I)-(N_2^{2-})-Fe(I) with a total spin of 2. However, the magnetic data collected contradicts this prediction by showing the complex to be essentially nonmagnetic. This could be accounted for by interpreting the Fe centers as low-spin d^7 metals (S=0.5 for each metal). Alternatively, broken symmetry DFT calculations suggest that the two Fe centers are anti-ferromagnetically coupled and that while the N_2 fragment does carry extra electron density, it is not magnetic. Thus, while we do not have clear experimental evidence on how to best describe the complex electronically, these results do clearly show that the electronic structure of this class of molecule can vary widely and is not necessarily identified through any single technique.

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References

[1] Peters, J. C.; Mehn, M. P. In *Bio-organometallic approaches to nitrogen fixation chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: 2006; pp 81-119.
[2] MacLeod, K. C.; et al., Nat. Chem., 5, 559-565 (2013).
[3] Rodriguez, M. M., et al., Science, 334, 780-783 (2011).
[4] Holland, P. L. Dalton Trans., 39, 5415-5425 (2010).