

ELECTRONIC AND STRUCTURAL PROPERTIES OF IRON COMPLEXES WITH FORMAZANATE LIGANDS

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Complexes that show spin-crossover are well known for 6-coordinate, octahedral geometries. Due to a much weaker ligand field in 4-coordinate complexes, these (with very few exceptions)^[1] lead to high spin-states only. Here, we present 4-coordinate iron(II) complexes with formazanate ligands (L_2Fe), some of which show spin-crossover. The strong π -acceptor properties of these ligands leads to an unusual d-orbital splitting pattern that stabilizes the low-spin ($S = 0$) state in these compounds.^[2] We investigated the effect of steric and electronic changes in the ligand framework and a range of spectroscopic, magnetic and computational techniques is used to understand the origin of spin-crossover in these compounds. The redox behavior of the bis(formazanate) iron complexes has also been studied by cyclic voltammetry and isolation and characterization of the reduced compounds ($Fe(I)$, $S = 1/2$) have been carried out. Furthermore, the reactivity of isocyanide with L_2Fe leads to the formation of an octahedral diamagnetic complex. Moreover, attempted oxidative addition of alkyl halides to the $Fe(I)$ complex $[L_2Fe]^-$ allows the isolation of a high-spin mono(formazanate) iron complex, for which a rational synthesis was developed.

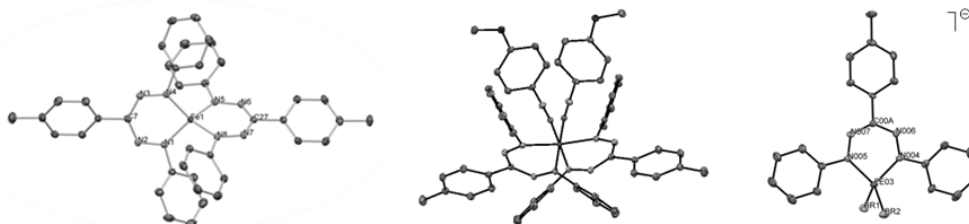


Figure1. Iron formazanate complexes.

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- 2) R. Travieso-Puente, J. O. P. Broekman, M.-C. Chang, S. Demeshko, F. Meyer, E. Otten, *J. Am. Chem. Soc.* **2016**, 138, 5503.