

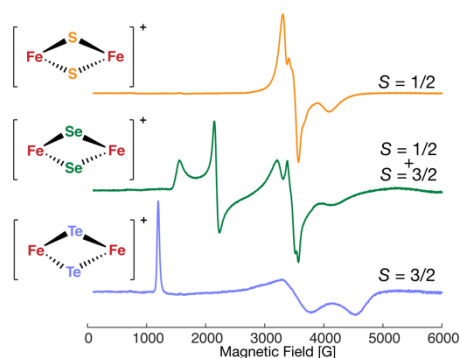
Stabilization of Intermediate Spin-States in Mixed-valent Diiron Dichalcogenide Complexes

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The electronic structure and ground spin-states observed for mixed-valent iron-sulfur dimers ($\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$) are typically determined by the Heisenberg exchange interaction, J , that couples the magnetic interaction of the two metal centers. These iron centers may be either ferromagnetically ($J > 0$) giving a total high-spin, $S = 9/2$, cluster, or anti-ferromagnetically coupled ($J < 0$) yielding a low-spin, $S = 1/2$, cluster. In the case of anti-ferromagnetically coupled iron centers, stabilization of the high-spin $S = 9/2$ ground state is also feasible through a Heisenberg double-exchange interaction, B .¹ This double-exchange interaction lifts the degeneracy of the Heisenberg spin-states and has been used to explain the presence of some $S = 9/2$ mutant ferredoxin clusters and other biomimetic models.^{2,3} This theorem also predicts intermediate spin-states, $S = 3/2$, $5/2$ and $7/2$, for mixed-valent $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ dimer but prior to our present study, had never been observed. Here, I will present the structural, electron paramagnetic resonance and Mössbauer spectroscopic, and magnetic characterization of a series of $[\text{Fe}_2\text{Q}_2]^+$ ($\text{Q}=\text{S}^{2-}$, Se^{2-} , Te^{2-}) mixed-valent complexes where Se and Te incorporation favors $S = 3/2$ spin-states.⁴ The incorporation of heavier chalcogenides in this series reveals the delicate balance of antiferromagnetic coupling, Heisenberg double-exchange, and vibronic coupling, providing fundamental insight into the factors that enable the stabilization of intermediate spin-states of mixed-valent dimers.



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⁴ Henthorn, J. T.; Cutsail, G. E.; Weyhermüller, T.; DeBeer, S., *Nature Chemistry* **2022**, 14 (3), 328-333.