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 (Fe\textsuperscript{II}-Fe\textsuperscript{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, $B$.\textsuperscript{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.\textsuperscript{2,3} This theorem also predicts intermediate spin-states, $S = 3/2$, 5/2 and 7/2, for mixed-valent Fe\textsuperscript{II}-Fe\textsuperscript{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 [Fe\textsubscript{2}Q\textsubscript{2}]\textsuperscript{+} (Q=S\textsuperscript{2–}, Se\textsuperscript{2–}, Te\textsuperscript{2–}) mixed-valent complexes where Se and Te incorporation favors $S = 3/2$ spin-states.\textsuperscript{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.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{Schematic representation of intermediate spin-states in mixed-valent diiron dichalcogenide complexes.}
\end{figure}

\begin{thebibliography}{9}
\bibitem{1} Sharma, S.; Sivalingam, K.; Neese, F.; Chan, G. K., \textit{Nat. Chem.} \textbf{2014}, \textit{6} (10), 927-933.
\bibitem{2} Achim, C.; Golinelli, M.-P.; Bominaar, E. L.; Meyer, J.; Münck, E., \textit{J. Am. Chem. Soc.} \textbf{1996}, \textit{118} (34), 8168-8169.
\bibitem{3} Ding, X. Q.; Bominaar, E. L.; Bill, E.; Winkler, H.; Trautwein, A. X.; Drueke, S.; Chaudhuri, P.; Wieghardt, K., \textit{J. Chem. Phys.} \textbf{1990}, \textit{92} (1), 178-186.
\bibitem{4} Henthorn, J. T.; Cutsail, G. E.; Weyhermüller, T.; DeBeer, S., \textit{Nature Chemistry} \textbf{2022}, \textit{14} (3), 328-333.
\end{thebibliography}