Magnetism of Mixed-valent Fe_8 Clusters, $[Fe_8(\mu_4\text{-}O)_4(\mu\text{-}4\text{-}Cl\text{-}pz)_{12}X_4]^-$.

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Introduction

The phenomenon of double exchange and its effect on the ordering of spin states in delocalized, mixed-valent transition metal complexes has been studied in detail in dinuclear systems. In contrast, there is a paucity of data for mixed-valent multinuclear clusters.

We have been studying the electronic structure of octanuclear iron-clusters, of formula $[Fe_8(\mu_4\text{-}O)_4(\mu\text{-}4\text{-}R\text{-}pz)_{12}X_4]$, $[Fe_8]$, which contain a Fe_4O_4-cubane core and four more outer Fe-centers.[1] One-electron reduction of these clusters yields their mixed-valent $[Fe_8]^-$ analogues, formally $Fe^{II}Fe_7^{III}$-clusters. The complete description of their magnetic properties involves the isotropic exchange parameters J_1, J_1' and J_2 (Fe^{III}-Fe^{III} and Fe^{II}-Fe^{III} within the cubane core and Fe^{II} core -Fe^{III} outer, respectively), the double exchange parameters t_1 and t_2 (cubane-cubane and cubane-outer, respectively), anisotropy and vibronic coupling. The overparameterization of the complete Hamiltonian for this system leads to several sets of solutions result in acceptable fitting the magnetic susceptibility plots.

Experimental

The magnetization vs. field plots of three different $[Fe_8]^-$ cluster (X = Cl, Br and NCS) were recorded at 1.5 K using the 0 - 95 T pulsed-magnet at LANL. Magnetization steps were detected at 70 T.

Results and Discussion

The ground state of the $[Fe_8]^-$ complexes has been previously determined by EPR spectroscopy to be S = 1/2. Therefore, the magnetization steps found here correspond to the crossover of the m_s -1/2 and -3/2 levels (**Figure 1**). The crossover at 72 T in turn corresponds to a 72 cm^{-1} gap separating the S = 1/2 and S = 3/2 states at 0 field.

Magnetic susceptibility vs. temperature plots (SQUID) were fitted varying systematically the values of sets of isotropic exchange and double exchange parameters using as starting points values calculated by DFT methods. Good fits that also reproduce the pulsed-field magnetization steps were achieved with a set of $J_1 = -6$ cm^{-1}, $J_1' = -10$ cm^{-1}, $J_2 = -55$ cm^{-1}, $t_1 = 1400$ cm^{-1} and $t_2 = \sim 0$.

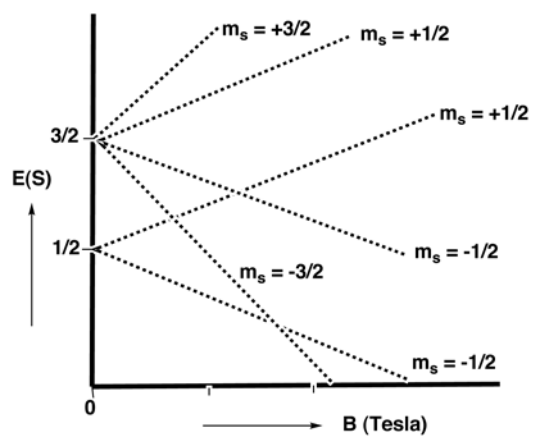

Figure 1. Splitting of of lowest two spin states of $[Fe_8]^-$ under the external pulsed magnetic field.

Conclusions

The magnetic response of a mixed-valent $[Fe_8]^-$-cluster has been explored using a combination of SQUID and high-field pulsed magnetometry and density functional theory. This has allowed an evaluation of the double exchange parameters among the four Fe-cubane centers of the octanuclear system.

Acknowledgements

This material is based upon work supported by the National Science Foundation under CHE-0822600.

References

[1] Chakraborty, I., *et al.*, Inorganic Chemistry, **47**, 11734-11737 (2008).