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

R.G. Raptis (Florida International U., Chemistry); R. McDonald, J. Singleton (NHMFL); J.E. McGrady (U. Oxford); R. Herchel (Palacký U.); E. Zueva (Kazan State Technological U.)

Introduction

The electron-transfer and magnetic properties of redox-modified iron oxide complexes are of interest because they relate to the analogous processes in bulk and nanoparticular iron oxides. We have been studying octanuclear iron-clusters of the general formula $[Fe_8(\mu_4\text{-}O)_4(\mu\text{-}4\text{-}R\text{-}pz)_{12}X_4]^z$, $[Fe_8]^z$, z = 0, 1–, 2–, which contain a Fe_4O_4-cubane core and four more outer Fe-centers. The same Fe_8O_4-motif is encountered in the all-ferric minerals maghemite (γ-Fe_2O_3) and ferrihydrite and the mixed-valent magnetite (Fe_3O_4). Analysis by a combination of spectroscopic techniques has shown that in the one-electron reduced $[Fe_8]^-$ complexes, an itinerant electron is delocalized primarily over the Fe_4O_4-cubane with less than 30% of electron density spilling out to the four outer Fe-sites at temperatures above 4 K. In contrast, in the $[Fe_8]^{2-}$ clusters, two itenerant electrons become localized at temperatures < 120 K.

Experimental

The magnetization vs. field plots of three different $[Fe_8]^{2-}$ cluster (X = Cl, Br and NCS) were recorded at 1.5 K using the 0 - 65 T pulsed-magnet at LANL. No magnetization steps were detected up to 65 T.

Results and Discussion

We have previously shown that $[Fe_8]^0$-complexes have a diamagnetic ground state whose separation from the first excited S = 1/2 state is reflected in a step at ~ 36 T in magnetic moment vs. magnetic field plots. The analogous $[Fe_8]^-$ species have a S = 1/2 ground state whose separation from the S = 3/2 corresponds to a step at ~63 T. In contrast, the doubly reduced $[Fe_8]^{2-}$ complexes (a) do not show a stepped magnetic moment profile at all and (b) the X = Cl and Br species are distinguished from the X = NCS by the different slope of their plots (Fig. 1). The analysis of pulsed magnetometry and SQUID data with the assistance of density functional theory calculations is in progress.

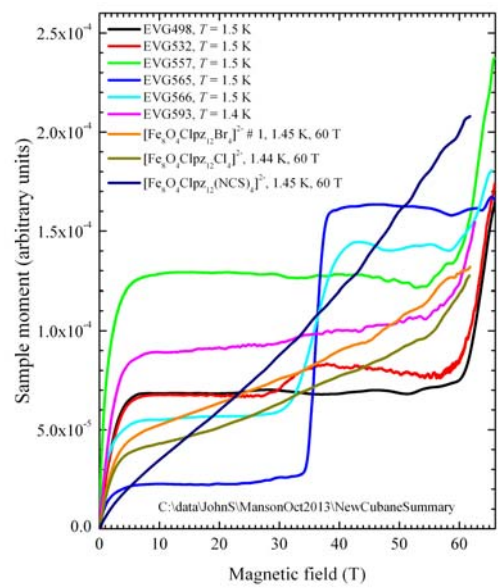

Figure 1. Magnetic moment vs. field plots of all-ferric $[Fe_8]^0$ and mixed-valent $[Fe_8]^-$ and $[Fe_8]^{2-}$ complexes. The new compounds studied in 2013 are the final three listed in the inset. Compounds studied in 2012 are shown for reference.

Conclusions

The magnetic response of mixed-valent $[Fe_8]^{2-}$-clusters has been explored using a combination of SQUID and high-field pulsed magnetometry. The distinct M(H) profile of each spin state is invaluable in identifying the underlying quantum behavior.

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