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Unraveling the Mechanism for Room Temperature Magnetism in V[TCNE]$_{x\sim2}$

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The molecule-based magnet V[TCNE]$_{x\sim2}$ exhibits magnetic order up to 400 K, magneto-resistance, and photo-induced magnetism. These properties imply a distinct, robust mechanism for magnetism, and yet the spin-polarized interactions between V and TCNE (C_6N_4) constituting this mechanism had remained elusive, in large part because the system has to date resisted crystallization. Recent spectroscopic studies [1] have shown that metals modify the molecular orbital (MO) structure of TCNE and suggested a covalent interaction between V and TCNE, but no specific mechanism had been proposed.

We have measured x-ray absorption spectra (XAS) and MCD at the V $L_{2,3}$ edges, and the C and N K edges in CVD films and isolated molecules to gain further insight into V[TCNE]$_{x\sim2}$ properties [2]. At the C and N edges we observe a spin-polarized splitting of the former lowest unoccupied MO, and otherwise that the MO structure remains largely intact. V XAS and MCD can be partially modeled assuming fully spin polarized V^{2+} in an octahedral ligand field using just the t_{2g} states, leaving an additional broad component to higher energy that cannot be well modeled with a single-state or charge-transfer multiplet model.

We interpret these results within a generalized bonding/backbonding model in which V is octahedrally coordinated by the terminal N in σ-bridging positions between TCNE$^{\bullet-}$ radical anions. The covalent interaction between the V e_g and TCNE π MO states holds the two species together [3], explains the excess V XAS intensity as an antibonding feature, and is not spin-polarized. The interaction between V t_{2g} and TCNE π MOs straddles the Fermi level, is spin-polarized, and couples net spin on TCNE$^{\bullet-}$ ferrimagnetically to that on V. Thus a direct exchange interaction between V and TCNE underlies the magnetic properties of V[TCNE]$_{x\sim2}$.

These results reveal an active role of the molecular constituent in this molecule based magnet, which is distinctly different from superexchange models generally assumed to describe such systems. In addition to demonstrating the first MCD spectra at the C K edge, these results show how it is possible to use element-resolved absorption spectroscopies to follow changes to the electronic structure of molecules as they assemble into molecule-based magnets.

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