Magnetically-Coupled Molecular Systems: Toward Conducting/Magnetic Hybrids

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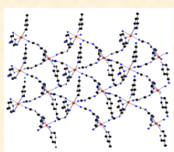
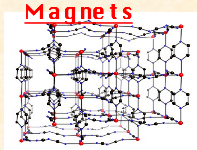
Introduction

A variety of new magnetic materials composed of molecular organic building blocks and spin bearing transition metal ions have been synthesized. These solid state materials have novel nanoscale structures that can be readily modified to tailor their magnetic properties. The dicyanamide anion, $[N(CN)_2]^-$, has been shown to be a versatile ligand for linking transition metals in two-dimensional arrays. These anionic networks are ideal building blocks for the self-assembly of new molecular superconductors, magnets and conducting/magnetic hybrid materials. Such multifunctional materials provide an exceptional opportunity for the incorporation of a variety of properties into the same material, which originate at the molecular and/or supramolecular level. We are initiating research on materials with hybrid properties, e.g., conducting/magnetic, conducting/optical etc.

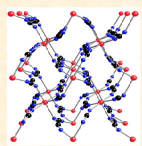
Neutral 2- and 3D Polymeric Metal-Dicyanamide Magnets



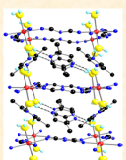
$Mn[N(CN)_2]_2(4\text{-}CNpy)_2$

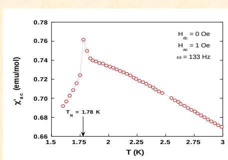


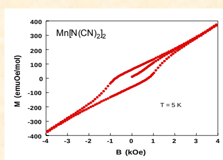
$Mn[N(CN)_2]_2(pyz)$



$Mn[N(CN)_2]_2$





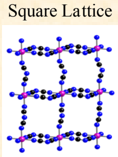


$Mn[N(CN)_2]_2(2,5\text{-}dimepyz)_2(H_2O)_2$

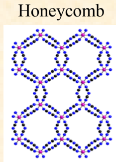
- Various 2- and 3D polymeric arrays can be obtained using mild synthetic conditions.
- Charge neutral systems are excellent model systems to probe lattice and spin dimensionality in molecular-based solids.
- Magnetic exchange interactions and critical temperatures are "tunable."
- Numerous types of magnetic phenomena have been observed in metal-dicyanamide materials such as weak ferromagnetism, ferromagnetism, antiferromagnetism, spin glasses and spin crossover.
- Particularly amenable to systematic investigations of structure-property correlations.

Anionic Molecular Building Blocks

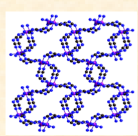
Square Lattice



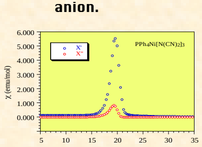
Honeycomb



3D



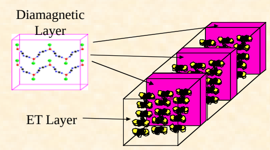
Three structural topologies of the $Mn[N(CN)_2]_3^-$ anion.

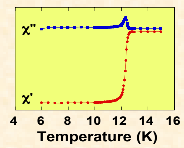


The PPh_4^+ salt of the $Ni[N(CN)_2]_3^-$ anion has been shown to exhibit ferromagnetic coupling.

- The dicyanamide anion, $[N(CN)_2]^-$, has been shown to be a versatile ligand for linking transition metals into various structural motifs.
- We have synthesized and characterized several such materials, including $PPh_4M[N(CN)_2]_3$ (M = Mn, Co, Ni and Hg).
- The resulting materials have novel nanoscale structures that can be readily modified to tailor their physical properties.

Highest-T_c Molecular Superconductor

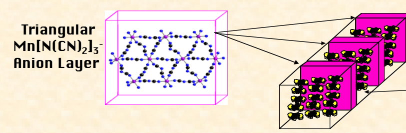




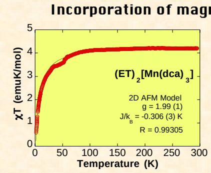
Molecular superconductors, $(ET)_2Cu[N(CN)_2]X$, (X = Cl, Br), with diamagnetic anion layers.

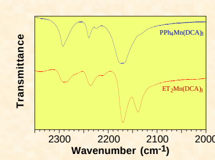
- The molecular superconductors with the highest superconducting transition temperatures, $(ET)_2Cu[N(CN)_2]X$ (X = Cl, Br), were discovered at ANL and serve as model compounds for hybrid materials.
- The ET donor layer is responsible for the superconducting behavior while the anion layer contains chains of diamagnetic Cu(I) ions.
- Our goal is to retain the structural features of the electron-donor layer while introducing magnetically active components into the anion layer.

Conducting/Magnetic Hybrid Molecular Solids



Incorporation of magnetic layer between ET donor layers





- Layered molecular solids that incorporate delocalized (conduction) and localized (magnetic) electrons are being investigated.
- We desire to gain an understanding of the factors related to self-assembly and the interplay of spin and electronic sublattices in molecular-based solids.
- We have recently successfully synthesized and characterized the $(ET)_2Mn[N(CN)_2]_3$ salt that contains a novel Kagomé lattice separated by conducting layers of ET radical cations. Incorporation of the $Mn(N(CN)_2)_3^-$ anion between conductive ET layers has resulted in a novel triangular (spin frustrated) magnetic anion layer, however, itinerant behavior has not been observed in this system.

Conclusions

We have shown that polymeric, non-magnetic, dicyanamide anions form superconducting salts when crystallized with the ET electron-donor molecule. We have developed an understanding of the factors influencing the self-assembly of transition metal dicyanamide anions.

Future Directions

Possible Compositions of Future Hybrid Materials

Layer 1	Layer 2	Material Properties
Conducting	Non-magnetic, closed shell Fixed valent	2D conductor, Superconductor
Conducting	Open shell, Mixed valent	High T_c superconductors
Conducting	Magnetic	Coupling of electronic and spin lattices: CMR, Spintronics
Conducting	Extended π-systems and dyes	Electron-exciton interactions: Photomodulation of electronic properties
Magnetic	Photochromic	Photomodulation of hysteresis loop.

The extension of this work to include the incorporation of magnetic dicyanamide anion layers into conducting charge transfer salts is expected to yield hybrid materials in which the delocalized (conduction) electrons are coupled with the localized electrons of the magnetic layer. Such materials are expected to find technological applications such as CMR devices and molecular electronics.

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