

Cyanide-Bridged Functional Fe Magnets with Mixed-Valence Structure

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博士論文の要約

Cyanide-Bridged Functional Fe Magnets With Mixed-Valence Structure

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Switchable molecular materials and single-chain magnets (SCMs) materials have attracted more and more attention owing their potential future applications as molecular switches and data storage devices. Our group has devoted years to this field, and a number of instances of spin-crossover (SCO), metal-to-ligand charge transfer (MLCT), metal-to-metal charge transfer (MMCT), SCMs and multifunction materials have been explored. From the viewpoint of controlling magnetic properties for multifunction materials, most of the published examples combine conductivity, ferroelectricity, and magnetic properties. For my work, I am interested in multifunction materials that combine of MMCT properties and SCMs. In order to obtain the materials which exhibit MMCT properties and SCMs, cyano-bridged system offer a great advantage for achieving such control. On the basis of the information outlined above, hydrotris(pyrazoylborate) (= Tp) was used to obtain novel Fe compounds exhibiting MMCT properties. In my thesis I show four novel Fe compounds with mixed-valence structure. All of my thesis comprise with 5 chapters.

Chapter 1, provides a brief description of the historical background of switchable multifunctional molecular magnets, and the scope of the work performed.

Chapter 2, the synthesis of the novel Fe(III)/Fe(II) mixed-valence one-dimensional coordination polymer $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]_2[\text{Fe}^{\text{II}}(\text{MeOH})_2] \cdot 2\text{MeOH} \cdot \text{H}_2\text{O}$ (Tp = hydrotris(pyrazoly) borate) is described. The structure of this complex was successfully determined by single-crystal X-ray analysis. The crystal structure of the complex consists of neutral cyanide-bridged chains. Within the neutral chain, the $[\text{Fe}(\text{Tp})(\text{CN})_3]^-$ unit acts as a bimonodentate ligand towards two Fe^{II} ions via two of its three cyanide groups. This arrangement, gives rise to cyanide-bridged one-dimensional double-zigzag chains. A study of the magnetic behavior of this complex showed a ferromagnetic interaction between the intrachain Fe^{III} and Fe^{II} ions and a weak antiferromagnetic interaction between the chains. In addition, the complex shows a field-induced transition from antiferromagnetic to ferromagnetic alignment between the chains, with the value of the critical field being *ca.* 2900 Oe at 2 K and *ca.* 1500 Oe at 3 K - 10 K. Furthermore, ac dynamic susceptibility measurements show strong frequency dependence at low temperature, suggesting that the complex is an

antiferromagnetic ordered phase of single-chain magnets.

Chapter 3, another novel Fe(III)/Fe(II) mixed-valence complex is introduced, namely $[\text{FeTp}(\text{CN})_3]_2\text{Fe}(\text{bpe}) \cdot 5\text{H}_2\text{O}$ (Tp = hydrotris(pyrazolyl)borate; bpe = 1,2-bis(4-pyridyl) ethane), which also contains a cyanide bridge. X-ray analysis of the crystal structure shows that the complex has a zigzag one-dimensional chain structure, which is further connected by a bpe ligand to form a network structure. Interestingly, the complex shows thermally-induced metal-to-metal charge transfer properties. It has an electronic structure of $\text{Fe}^{\text{III-LS}}\text{-CN-Fe}^{\text{II-HS}}\text{-NC-Fe}^{\text{III-LS}}$ at room temperature. On cooling, an electron transfer from $\text{Fe}^{\text{II-HS}}$ to $\text{Fe}^{\text{III-LS}}$ occurs at around 220 K. The low-temperature phase exhibits an electronic structure of $\text{Fe}^{\text{III-LS}}\text{-CN-Fe}^{\text{III-HS}}\text{-NC-Fe}^{\text{II-LS}}$. The thermally induced charge transfer at 220 K can be expressed by $\{[\text{Fe}^{\text{III-LS}}(\text{Tp})(\text{CN})_3]_2\text{Fe}^{\text{II-HS}}(\text{bpe})\} \cdot 5\text{H}_2\text{O} \leftrightarrow \{[\text{Fe}^{\text{II-LS}}(\text{Tp})(\text{CN})_3][\text{Fe}^{\text{III-LS}}(\text{Tp})(\text{CN})_3]\text{Fe}^{\text{III-HS}}(\text{bpe})\} \cdot 5\text{H}_2\text{O}$. The transition between the two states was confirmed by variable temperature IR spectroscopy, X-ray analysis, and Mossbauer spectroscopy. The magnetic interaction within the chain is ferromagnetic, where the interaction between the chains is anti-ferromagnetic. Anti-ferromagnetic ordering was observed at 15 K. The field-dependent magnetic behavior at 2 K showed that the complex is a meta-magnet. Furthermore, when ac dynamic susceptibility measurements were performed the material exhibited frequency dependence, suggesting that the complex is an antiferromagnetic ordered phase of SCMs.

Chapter 4 the synthesis of two novel Fe(III)/Fe(II) mixed-valence complexes with Tp ligand and tpy ligand, and $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]_2[\text{Fe}^{\text{II}}(\text{MeOH})_4] \cdot 2\text{MeOH}$ are described. The crystal structure of $[\text{Fe}^{\text{II}}(\text{tpy})_2][\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]_2 \cdot 2\text{MeOH}$ consists of a six-nitrogen-coordinate iron(II) cation, two $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]^-$ anions and two crystallization methanol molecules. The X-ray analysis of $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]_2[\text{Fe}^{\text{II}}(\text{MeOH})_4] \cdot 2\text{MeOH}$ shows that two $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]^-$ anions are bridged by $[\text{Fe}^{\text{II}}(\text{MeOH})_4]^{2+}$ cation forming a trinuclear unit, which is further connected between each other by uncoordinated methanol with hydrogen bonds to form a three-dimensional supra-molecule. The magnetic property shows that $[\text{Fe}^{\text{II}}(\text{tpy})_2][\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]_2 \cdot 2\text{MeOH}$ consists of one LS Fe(II) ion and two LS Fe(III)

ions with $t_{2g}^6e_g^0$ ($S = 0$) and $t_{2g}^5e_g^0$ ($S = 1/2$) spin states, respectively.

A summary of the work is given in Chapter 5 along with a discussion of the future prospects for this research area.