

Fundamental Study on Spin State Transition of Fe and Co Complexes

李, 国玲

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氏 名 : 李 国玲

Name

論 文 名 : Fundamental Study on Spin State Transition of Fe and Co Complexes
(鉄錯体とコバルト錯体のスピン状態転移に関する基礎研究)

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論 文 内 容 の 要 旨

Thesis Summary

Spin state transitions are significant for switchable physical properties, and spin state transitions can be achieved through several different magnetic dynamics, such as spin orientation flipping, spin number change. Importantly, these spin variation behaviors are deeply influenced by the molecular components, molecular structures and intermolecular interactions, which can be carefully adjusted via artful chemical modulation and synthesis controlment. Our group is focusing on the realization of spin state transitions in coordination compounds, and the revelation of the correlation of magnetic properties and molecular structures. Up to now, lots of coordination complexes that feature interesting spin state transitions, and thus showing switchable magnetic properties under external stimuli, have been developed by our group members. In this thesis, I carried out the present research work as a prolongation of our previous investigation, which will be discussed in the following content.

In **chapter 1**, the research background on spin state transitions and scope of my research work is briefly introduced.

In **chapter 2**, an octa-coordinated Fe(II) complex, $[\text{Fe}^{\text{II}}(\text{dpphen})_2](\text{BF}_4)_2 \cdot 1.3\text{H}_2\text{O}$ (dpphen = 2,9-di(pyrazo-1-yl)-1,10-phenanthroline) with a pseudo- D_{2d} symmetric metal center showing slow magnetic relaxation is reported. This Fe(II) complex slow magnetization dynamic (single-ion magnet, SIM) behavior since this it possesses strong uniaxial magnetic anisotropy. The uniaxial magnetic anisotropy for this high-coordinated Fe(II) is confirmed by magnetic measurement, high-frequency/field electron paramagnetic resonance (HF-EPR) studies, and *ab initio* calculations, which reveal that it has a negative axial zero-field splitting ($D \approx -6.0 \text{ cm}^{-1}$) and a small rhombic zero-field splitting ($E \approx 0.04 \text{ cm}^{-1}$). Under applied dc magnetic fields, the octa-coordinated Fe(II) complex exhibits SIM behavior at low temperature. Fitting the relaxation

time with the Arrhenius mode combining Orbach and tunneling terms affords a good fit to all the data and yields an effective energy barrier (17.0 cm^{-1}) close to the energy gap between the ground state and the first-excited state. The origin of the strong uniaxial magnetic anisotropy for this complex has been clearly understood from theoretical calculations.

In **chapter 3**, in order to observe charge transfer coupled spin transition (CTCST) behavior in cyanide-bridged $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$, ligand (1,4-(1H-1,2,4-triazole)butane, btb) with stronger π -acceptor ability has been used. Two new cyanide-bridged $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ mixed-valence compounds are presented, which were obtained via cyanoferrate $([\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]^-)$, Tp = hydrotris(pyrazolyl)borate and flexible ligand btb under different synthesis conditions. One of these two new compound $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2\text{Fe}(\text{btb})\cdot\text{H}_2\text{O}\}_n$ is a cyanide-bridged one-dimensional $\{\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\}_n$ double-zigzag chain, and exhibits thermal and photo-induced spin transition behavior in the $\text{Fe}(\text{II})$ sites. Whereas the other compound $[\text{Fe}(\text{Tp})(\text{CN})_3]_2\text{Fe}(\text{btb})_2\cdot 2\text{H}_2\text{O}$ features cyanide-bridged trinuclear linear $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$ motifs further linked by btb forming an extended linear chain, and shows weak antiferromagnetic interactions between metal centers. These results suggest that flexible ligands are sensitive to synthesis conditions and can be used to produce variable structures and magnetic properties. Although CTCST behavior has not been observed, the proposal for doing further work was provided, namely the ligand field strength and redox potential for the metal center should be carefully balanced via using ligand with moderate π -acceptor ability.

In **chapter 4**, collective spin number variation induced water-tunable thermal hysteresis in a valence tautomeric dinuclear cobalt complex $\{[\text{Co}(\text{tpa})_2](\text{dhbq})\}(\text{PF}_6)_3$ (tpa = tris(2-pyridyl)methylamine, dhbq = deprotonated 2,5-dihydroxy-1,4-benzoquinone) are introduced. Two polymorphs of complex $\{[\text{Co}(\text{tpa})_2](\text{dhbq})\}(\text{PF}_6)_3$ were obtained via controlling the recrystallization temperature. Importantly, the two polymorphs display very distinct magnetic behaviors, thus provide a good opportunity for the investigation on the “pure” contribution of intermolecular factors to the valence tautomeric behaviors. The polymorph with the $\{[\text{Co}(\text{tpa})_2](\text{dhbq})\}$ cations arranged *head-to-tail* characterizes relatively strong $\pi\cdots\pi$ interactions, and thus shows an abrupt and complete thermal valence tautomeric transition with adjustable hysteresis loop at around room temperature. Whereas, the polymorph featuring valence tautomeric cations arranged *head-to-waist* with their neighbors exhibits weak $\pi\cdots\pi$ interactions, thus lead to a gradual and incomplete thermal valence tautomeric transition. The valence tautomeric transition process for both polymorphs can be induced by light, but the light-excited states for them show distinct thermal relaxation behaviors.