Dynamics and Mechanism of Spin-State Interconversion

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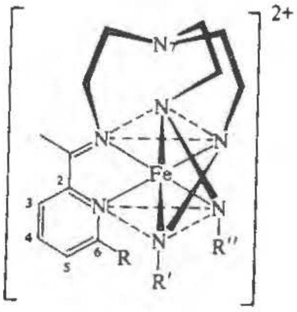
In an O_h ligand field, transition metal ions with d^4-d^7 electron configurations are capable of having a high-spin or low-spin configuration as ground state, depending on the ligand field splitting between the two spin states relative to the average electron pairing energy. When the ligand field strength is comparable to the electron pairing energy, a minor perturbation on external parameters such as temperature and pressure can change the ground state. This phenomenon is the so called spin-crossover transition [1].

Early research efforts were mainly focused on synthesizing new spin-crossover compounds and characterizing their bulk spin-state transformation properties. Even though the search for new spin-crossover complexes is still continuing, more efforts have been devoted to understanding the relationship between the spin-crossover transition, the cooperativity of the transition and the lattice properties [2]. Only recently, has closer attention been paid to the dynamics of the spin-state interconversion process [3]. The fact that little is known about the mechanism of the spin-state interconversion motivated us to investigate the dynamics of the process.

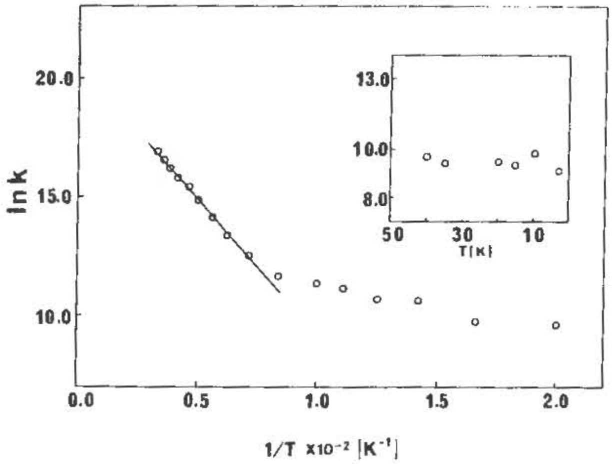
A series of ferrous spin-crossover complexes (see a), $[Fe(6\text{-}Me\text{-}py)_n(py)_{3-n}tren](ClO_4)_2$ (n=0,1,2,3), where the ligand is a Schiff base condensed from one mole of tris(aminoethyl)amine(tren) with n moles of 6-methyl-2-pyridinecarboxaldehyde and 3-n moles of 2-pyridinecarboxaldehyde, were characterized in the solid and solution states as well as diluted in polystyrene sulfonate polymer. In the solid state, complexes with n=1,2,3 exhibit a gradual spin-crossover transition while the complex with n=0 remains in the low-spin configuration up to 340K. At any temperature point in the transition temperature range, the high-spin fraction decreases with the value of n. In other words, the critical temperature increases when less methyl substituted 2-pyridinecarboxaldehyde is used in the Schiff base condensate. The observation of separate signals for low-spin and high-spin complexes in the ^{57}Fe Mössbauer spectra indicates that these complexes interconvert between the two spin states slowly relative to the Mössbauer time scale. In solution, the complex with n=3 is totally in the high-spin state down to 180K while the complex with n=0 is totally in the low-spin state at room temperature. The complexes with n=1 and n=2 exhibit a spin-equilibrium as evidenced by variable temperature UV-Vis spectra.

By employing the laser-flash photolysis technique, the spin-state interconversion rates of the complex with n=2 in solutions of acetone, acetonitrile, dichloromethane, methanol and toluene/acetonitrile(2:1) have been measured in the temperature range from room temperature to the freezing point of the solutions. The temperature dependence of the relaxation constants in these solutions follows the Arrhenius relationship. The apparent activation energy derived from the Arrhenius plots shows a strong solvent dependence. In a common solvent, the apparent activation energy varies among the complexes with different n due to the differences in the zero-point energy separations. In other words, the apparent activation energy decreases as the zero energy separation increases. From this, we can conclude that the spin-state interconversion dynamics is in the so called normal region [4].

When the complex with n=2 is doped into the matrix of the polystyrene sulfonate film, the low-spin state is stabilized, and consequently, the high-spin state of the complex cannot be thermally populated even at 340K. The rate constants from high-spin to low-spin relaxation have been measured in the temperature range of 300K-4.2K. The relaxation rate remains relatively constant below 120K (see b). The experimental data can be well fit to either of the theoretical models developed by Hopfield [5] or Jortner [6]. The theoretical study indicates that the spin-state conversion for this complex is due mainly to quantum mechanical tunneling not only in the 4.2-120K range but also in the 120-300K range.



(a)



(b)

Several research groups have proposed that an order-disorder transition associated with lattice solvate molecules may be responsible for triggering the spin-crossover transition [7]. In order to investigate this we studied the molecular dynamics of the solvate CD_3COCD_3, CD_2Cl_2 and $CDCl_3$ molecules in the lattice of the spin-crossover ferrous complex $Fe(dppen)_2Cl_2$, where dppen is cis-1,2-bis(diphenylphosphino)ethylene, by employing variable temperature powder ^2H NMR spectroscopy. The spin-crossover behavior of these three solvates and their regular hydrogen solvates were also characterized with magnetic susceptibility measurements, ^{57}Fe Mössbauer spectroscopy and the DSC thermal analysis technique. The variable temperature powder ^2H NMR spectra of $[Fe(dppen)_2Cl_2]\cdot 2CD_3COCD_3$ and $[Fe(dppen)_2Cl_2]\cdot 2CD_2Cl_2$ revealed that the solvate molecules undergo order-disorder transitions at the spin-crossover temperatures. The thermal effects derived from the DSC thermograms also support this interpretation.

A number of recent reports [8] have shown that some ferric spin-crossover complexes with N_4O_2 ligand atoms can interconvert between the two spin states in the solid state rapidly compared to the Mössbauer time scale. It was also reported that the spin-state interconversion rate is very sensitive to lattice solvation. The spin-crossover complex $[Fe(3\text{-}OMeSalAPA)_2]ClO_4$ has been synthesized and characterized with EPR spectroscopy, ^{57}Fe Mössbauer spectroscopy, magnetic susceptibility measurements and the DSC thermal analysis technique. The unsolvated form exhibits a very gradual spin-crossover transition. The observation of distinctive signals indicates a slow spin-state interconversion rate relative to the EPR time scale. However, the spin-state interconversion rate shows temperature dependence in the Mössbauer spectra. Above ca. 270K, the spin-crossover molecules interconvert between the two spin-states rapidly relative to the Mössbauer time scale. Below 270K, two distinctive doublets have been observed which indicates a slow spin-state interconversion rate. Upon solvation with C_6H_6, C_6H_5Cl, C_6H_5Br, $O-C_6H_4Cl_2$ the bulk spin-state transformation of the ferric complex becomes more abrupt. The interconversion rates for all of these solvates fall in between the Mössbauer time scale and that associated with EPR spectroscopy.

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