Recent Research at Toyota Riken

Norimichi Kojima

[Study on the dynamical spin equilibrium and its induced successive magnetic phase transition]

In general, the Fe^{III} site coordinated by six S atoms is in the low-spin (LS) state, while the Fe^{III} site coordinated by six O atoms is in the high-spin (HS) state. Therefore, it is expected that the spin state of Fe^{III} coordinated by three S atoms and three O atoms is situated in the spin-crossover region. Actually, the spin equilibrium in which the high-spin (HS) state and the low-spin (LS) state exchange have been confirmed for mononuclear Fe^{III} complexes consisting of $Fe^{III}O_3S_3$. However, the rapid spin equilibrium phenomenon has not yet been observed for assembled metal complex systems. From this viewpoint, in order to build an assembled metal complex system including $Fe^{III}O_3S_3$ site, we have synthesized $Ph_4P[Zn^{II}Fe^{III}(mto)_3]$ (mto = monothiooxalato) consisting of $Fe^{III}O_3S_3$ and $Zn^{II}O_6$ octahedra and investigated the spin state of the $Fe^{III}O_3S_3$ site. $Ph_4P[Zn^{II}Fe^{III}(mto)_3]$ has a two-dimensional honeycomb network structure.

The ESR signals corresponding to the HS state and the LS state of Fe^{III} site were observed at about 300 mT ($g \approx 2.05$) and at about 150 mT ($g \approx 4.25$), respectively, in the temperature range between 10 and 300 K. The ESR signal ratio of the LS state to the HS state increases with decreasing temperature, which indicates that the spin state of $Fe^{III}O_3S_3$ is the spin equilibrium between the HS and LS states, where the HS and LS states are clearly distinguishable in the time scale (10^{-10} s) of ESR spectroscopy.


Dynamical spin-equilibrium at $Fe^{III}O_3S_3$ in $Ph_4P[Zn^{II}Fe^{III}(mto)_3]$ (mto = C_2O_3S)
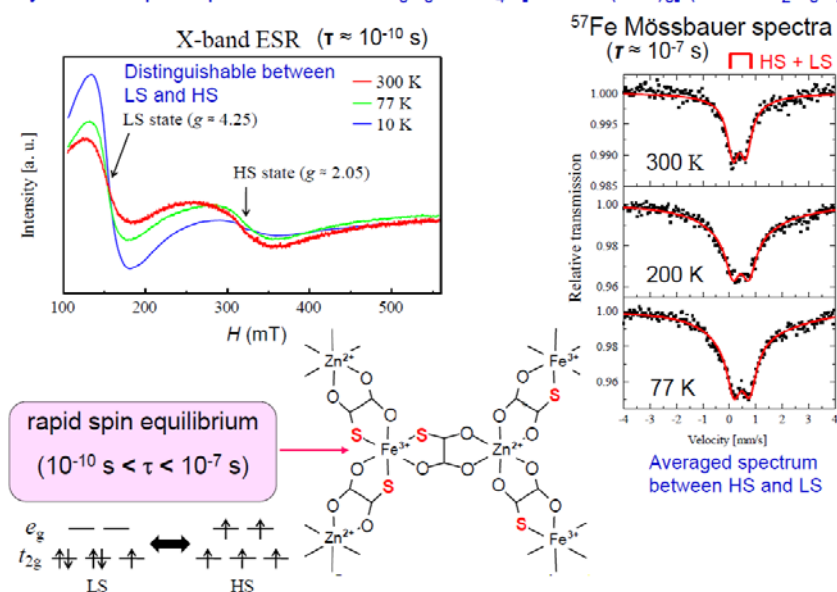
On the other hand, in the ^{57}Fe Mössbauer spectra of Ph$_4$P[Zn^{II}Fe^{III}(mto)$_3$] at 300, 77 and 10 K, a single quadrupole doublet of Fe^{III} was observed despite of the coexistence of the HS and LS states in the ESR measurement between 10 and 300 K. Therefore, the ^{57}Fe Mössbauer spectra of Ph$_4$P[Zn^{II}Fe^{III}(mto)$_3$] indicates that the rapid spin equilibrium between the HS and LS states occurs in the time scale faster than 10^{-7} s at the Fe^{III}O$_3$S$_3$ site. Therefore, the time scale of spin equilibrium of Fe^{III} in Ph$_4$P[Zn^{II}Fe^{III}(mto)$_3$] is estimated at $10^{-10} < \tau < 10^{-7}$ s from the analysis of ESR and ^{57}Fe Mössbauer spectroscopy.

In the case of [Mn^{II}Fe^{III}(mto)$_3$](mto = C$_2$O$_3$S) complex consisting of Fe^{III}O$_3$S$_3$ and Mn^{II}O$_6$ octahedra, there exists a dynamical spin equilibrium ($\tau < 10^{-7}$ s) between the high-spin and low-spin states at the Fe^{III}O$_3$S$_3$ site, which induces the frustration of internal magnetic field between the ferromagnetic and antiferromagnetic interactions on the Mn^{II} site. Figure shows the schematic representation of the dynamical spin equilibrium between the high-spin and low-spin states at the Fe^{III}O$_3$S$_3$ site and the frustration of internal magnetic field between the ferromagnetic and antiferromagnetic interactions on the Mn^{II} site for [Mn^{II}Fe^{III}(mto)$_3$] complex.

Spin state of (C$_6$H$_5$)$_4$N[Mn^{II}Fe^{III}(mto)$_3$] (mto = C$_2$O$_3$S)
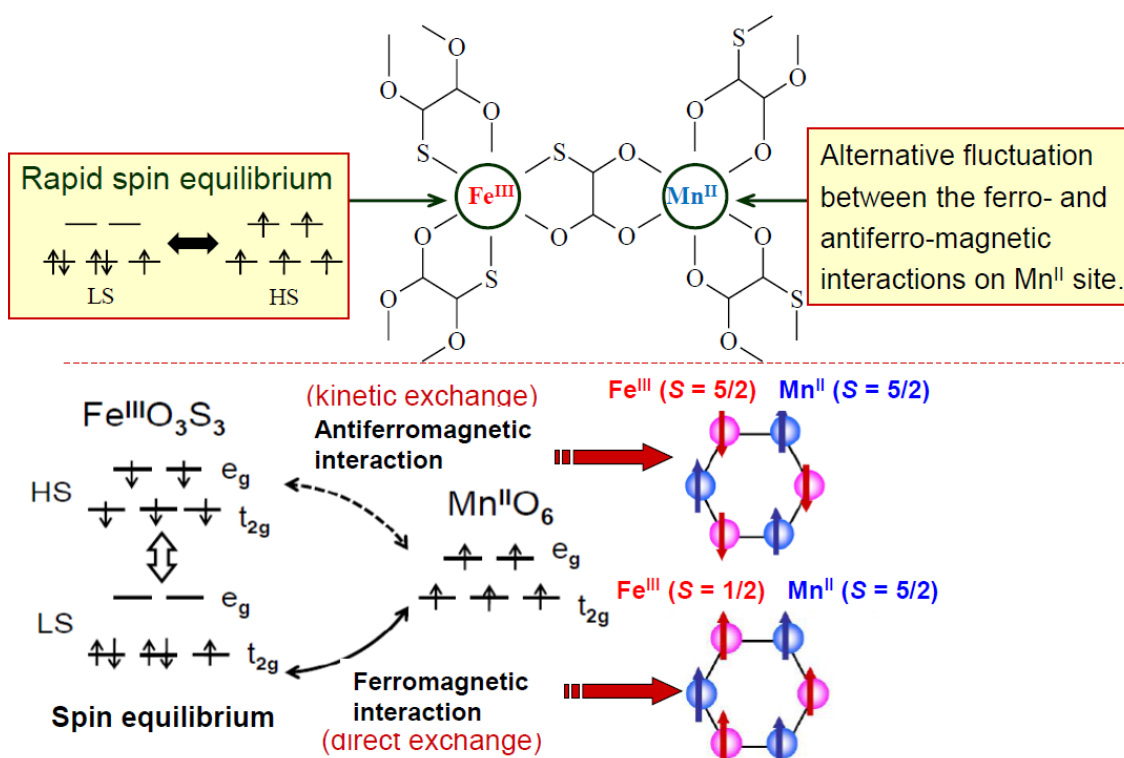
From this viewpoint, we have synthesized a mto (= C$_2$O$_3$S) bridged hetero-metal complex system, (C$_6$H$_5$)$_4$P[Mn^{II}Fe^{III}(mto)$_3$] consisting of Fe^{III}O$_3$S$_3$ and Mn^{II}O$_6$ octahedra.

The molar magnetic susceptibility (χ_M) as a function of temperature has a broad maximum, typical character of 2D Heisenberg-type antiferromagnet, around 50 K, and shows a steep increase below 30 K with a hump around 23 K, where both of the real (χ') and imaginary (χ'') parts in AC magnetic susceptibility exhibit steep peaks indicating a magnetic phase transition. The field cooled magnetization shows a rapid increase below 30 K, and almost saturares below 23 K. At 30 K, the remnant magnetization and the magnetic hysteresis loop disappear. Therefore, it is obvious that $(C_6H_5)_4P[Mn^{II}Fe^{III}(mto)_3]$ undergoes two successive magnetic phase transitions at 30 K and 23 K. The ^{57}Fe Mössbauer spectroscopy for $(C_6H_5)_4P[Mn^{II}Fe^{III}(mto)_3]$ implies that the spin state at the Fe^{III} site is still paramagnetic even at 24 K. At 23 K, both of the Mn^{II} and Fe^{III} spins are eventually ordered. It is considered that the successive magnetic phase transitions in $(C_6H_5)_4P[Mn^{II}Fe^{III}(mto)_3]$ are induced by the rapid spin equilibrium at the Fe^{III} site.
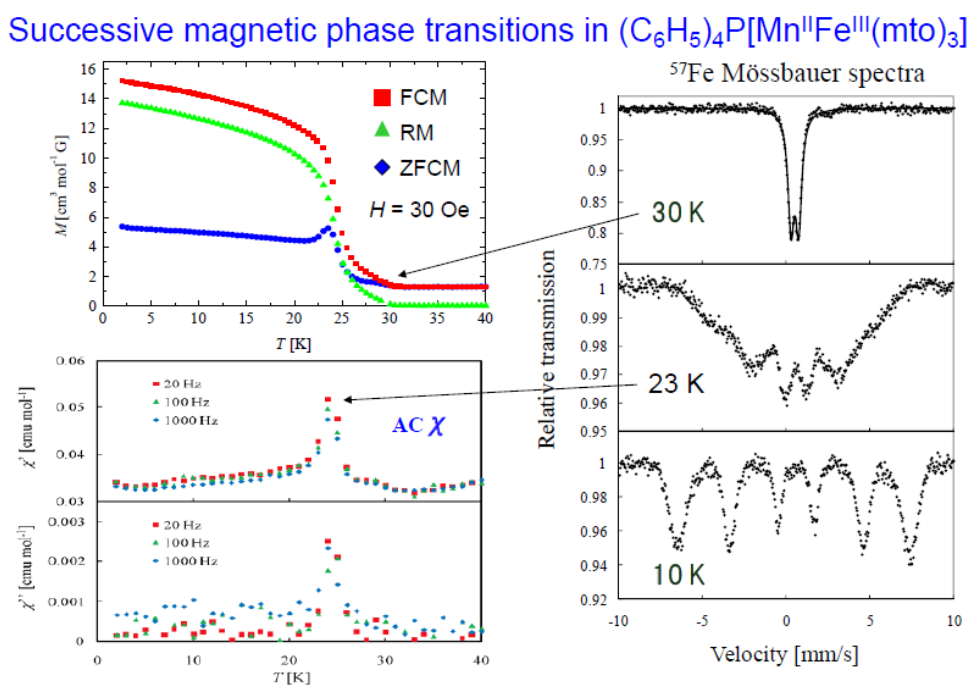

Figure: Successive magnetic phase transitions induced by the rapid spin equilibrium of $Fe^{III}O_3S_3$ site for $(C_6H_5)_4P[Mn^{II}Fe^{III}(mto)_3]$.

[pH-responsive spin-crossover complex film, [Fe^{II}(diAMsar)]-Nafion]

We have developed pH-responsive spin-crossover Fe^{II} complex films, by using diAMsar (1,8-diaminosarcophagine) as a ligand. Sarcophagine (sar) and its derivatives are hexadentate cage-type ligands, whose coordination compounds with Fe^{II} exhibit the

spin-crossover phenomenon between the high spin state with $t_{2g}^4 e_g^2$ ($S = 2$) and the low spin state with t_{2g}^6 ($S = 0$). The spin-transition temperature and the color of [Fe^{II}(diAMsar)] in the solution depend on pH ($T_{1/2} = 290$ K for pH = 4.5; $T_{1/2} = 370$ K for pH = 8.5) due to the protonation/deprotonation of the terminal amino groups in diAMsar. [Fe^{II}(diAMsar)]-Nafion also has different colors depending on the proton concentration controlled by buffer solution (pH = 4, 7 and 10). In acidic condition, the volume of [Fe(II)(diAMsar)] complex would be expanded due to the electrostatic repulsion between the Fe(II) ion and the NH$_3^+$ groups in diAMsar derived from the protonation of terminal amino groups, thus the strength of ligand field becomes weak, leading to the predominant high spin component of $t_{2g}^4 e_g^2$ ($^5T_{2g}$, $S = 2$) for Fe(II). On the other hand, in basic condition, the low spin component of t_{2g}^6 ($^1A_{1g}$, $S = 0$) is predominant because such a volume expansion is absent due to the deprotonation of the NH$_3^+$ groups in diAMsar. This pH-responsive spin-crossover phenomenon indicates that the spin state of [Fe^{II}(diAMsar)]-Nafion can be spatiotemporally manipulated by the gradient of proton concentration derived from applied voltage. In this way, we can visualize the proton flow in Nafion membrane by using the pH-responsive spin-crossover complex as a color indicator. The development of field responsive spin-crossover complex films will open a large field of multifunctional molecular devices based on Nafion membrane.