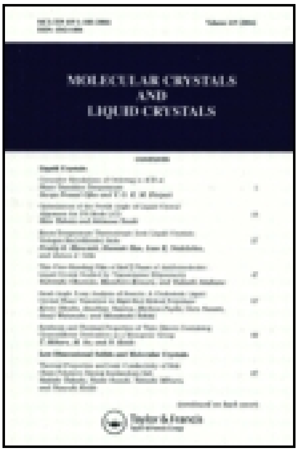

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[a] Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Tokyo, 153-8902, Japan

[b] Research Reactor Institute, Kyoto University, Osaka, 590-0494, Japan

[c] Department of Chemistry, Graduate school of Science, The University of Tokyo, Tokyo, 113-0033, Japan

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Search on Multi-Functional Properties of Spin-Crossover System

NORIMICHI KOJIMA[a], SHUJI TOYAZAKI[a], MIHO ITOI[a], YUUKI ONO[a], WATARU AOKI[a], YASUHIRO KOBAYASHI[b], MAKOTO SETO[b] and TOSHIHIKO YOKOYAMA[c]

[a]*Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Tokyo 153-8902, Japan,*
[b]*Research Reactor Institute, Kyoto University, Osaka 590-0494, Japan and*
[c]*Department of Chemistry, Graduate school of Science, The University of Tokyo, Tokyo 113-0033, Japan*

We have investigated the spin-crossover behavior for one-dimensional complexes $[Fe(trz)_3](RSO_3)_2$(trz= triazole) and two-dimensional mixed-valence complexes $(C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (dto= $C_2O_2S_2$). For the case of $[Fe(4\text{-}NH_2trz)_3](RSO_3)_2$, we have controlled Tc and the thermal hysteresis width of spin transition by using the isomerization of counter anion or the fastener effect between the alkyl chains of counter anions $C_nH_{2n+1}SO_3^-$. Moreover, we have synthesized a $[Fe(Htrz)_3]$ film by using an ion-exchange film having SO_3^-, which shows the spin transition around room temperature. For the case of $(C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$(n = 3,4), we have found a charge transfer phase transition between Fe^{II} and Fe^{III} around 120 K.

Keywords: spin crossover; ferromagnetism; mixed-valence; charge transfer phase transition; fastener effect

INTRODUCTION

Transition metal complexes with d^4-d^7 have a possibility of spin transition between the low-spin (LS) and the high-spin (HS) states. In particular, various kinds of Fe^{II} complexes show the spin transition between the diamagnetic state (S= 0) and the paramagnetic state (S= 2)[1]. Among these Fe^{II} complexes, recently, the photo-induced spin transition(called LIESST= Light Induced Excited Spin State trapping) has been reported at low temperatures for $[Fe(ptz)_6](BF_4)_2$[2], $[Fe(2\text{-}pic)_3]Cl_2 \cdot EtOH$[3], etc. On the other hand, Fe^{II} complexes coordinated by triazole (trz) are known to show the spin transition with a large thermal hysteresis around room temperature[4]. These phenomena are quite important properties from the viewpoint of molecular devices.

Recently, we have systematically investigated spin-crossover phenomena for one-dimensional complexes $[Fe(4\text{-}NH_2trz)_3]$ $(RSO_3)_2$ and two-dimensional mixed-valence complexes $(C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$(dto= $C_2O_2S_2$). In this paper, we report the spin crossover phenomena and the multi-functional properties for these complexes.

EXPERIMENTAL RESULTS AND DISCUSSION

Spin crossover phenomena for $[Fe(4\text{-}NH_2trz)_3]$ $(RSO_3)_2 \cdot 2H_2O$

Fe^{II} complexes coordinated by 1,2,4-triazole and its derivatives are known to form the triazole-bridged Fe chain structure illustrated in Fig. 1 and to show the spin transition with a large thermal hysteresis around room temperature[4]. The transition temperature (Tc) and the hysteresis width depend on not only ligand molecule but also counter anion and crystal water[5-7]. In order to control Tc and the hysteresis width, we have investigated the spin crossover phenomena for $[Fe(4\text{-}NH_2trz)_3](C_mH_{2m+1}SO_3)_2 \cdot 2H_2O$.

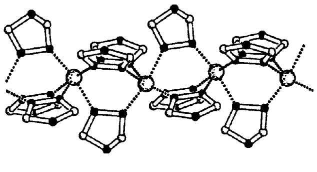


FIGURE 1. Fe chain structure of $[Fe(trz)_3]$ complex. Large circle: Fe, small circle: C, black filled circle: N.

Figure 2 shows the transition temperature (Tc) between the low-spin state (S= 0) and the high-spin state (S= 2) for $[Fe(4\text{-}NH_2trz)_3](C_mH_{2m+1}SO_3)_2{\cdot}2H_2O$(m=1-9). As shown in Fig. 2, Tc becomes higher by 80 K with increasing the length of alkyl chain of the counter anion, then it saturates at m>5. In connection with this, the following should be mentioned. In the case of $[Fe(trz)_3]$ complexes having isotropic counter anions such as BF_4^-, Tc decreases linearly with increasing the radius of counter anion[6]. In the case of the hysteresis width of spin transition, it decreases with increasing the length of counter anion. In order to elucidate the effect of the length of counter anion on Tc and the hysteresis width, we have investigated the Fe K-edge EXAFS spectra. According to the EXAFS spectra, the first nearest neighbor Fe-N distance does not depend on the length of the counter anion. The first nearest neighbor Fe-N distances in the low-spin and the high-spin states are 1.99-2.00Å and 2.17-2.18Å, respectively, for $[Fe(4\text{-}NH_2trz)_3](C_mH_{2m+1}SO_3)_2{\cdot}2H_2O$(m=1-9). On the other hand, the Fe-Fe distance becomes shorter with increasing the length of counter anion. From the analysis of EXAFS spectra, the following is concluded. As the length of the counter anion increases, the van der Waals' force between the alkyl chains of counter anions increases because of "fastener effect", which shorten the Fe-Fe distance and increase the elastic energy. Consequently, the transition temperature increases with increasing the length of counter anion.

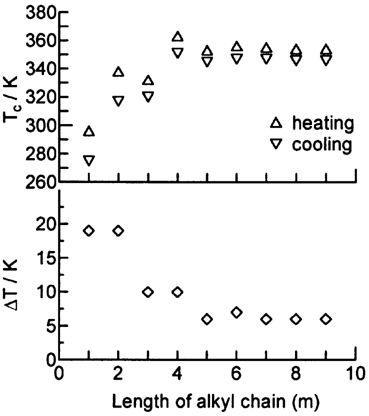


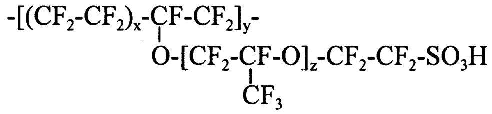
FIGURE 2. Tc and the hysteresis width versus the length (m) of counter anion of $[Fe(4\text{-}NH_2trz)_3](C_mH_{2m+1}SO_3)_2{\cdot}2H_2O$.

Moreover, we have investigated the effect of structural isomerism of counter anion on Tc and the hysteresis width for $[Fe(4\text{-}NH_2trz)_3]$(*o*-, *m*-, *p*-$NH_2C_6H_4SO_3)_2 \cdot 2H_2O$. In the case of *o*-salt, with increasing temperature, an abrupt spin transition occurs at 341 K. In the cooling process, the spin transition with thermal hysteresis of 9 K occurs abruptly at 332 K. In the case of *m*-salt, with increasing temperature an abrupt spin transition occurs at 331 K. In the cooling process, the spin transition with wide hysteresis of 26 K occurs abruptly at 305 K. In the case of *p*-salt, with increasing temperature, the spin transition occurs stepwise around 240 K and 310 K. In the cooling process, the spin transition occurs also stepwise around 290 K and 230 K. The two-step spin transition would be attributed to two non-equivalent lattice sites of Fe^{II}. In this way, we have found that Tc and the hysteresis width of $[Fe(4\text{-}NH_2trz)_3]$(*o*-, *m*-, *p*-$NH_2C_6H_4SO_3)_2 \cdot 2H_2O$ are drastically varied by the isomerization of counter anion.

Spin-Crossover Complex Film Based on $[Fe(trz)_3]$

Spin crossover complexes, $[Fe(4\text{-}NH_2trz)_3](RSO_3)_2 \cdot nH_2O$, show the abrupt spin transition with a large thermal hysteresis around room temperature, which has a possibility of some molecular devices such as display and memory. In order to realize photo-sensitive molecular devices, the synthesis of single crystal or transparent film is indispensable. Recently, we have synthesized several $[Fe(4\text{-}Rtrz)_3]$ complex films by using ion-exchange films as counter anion.

Nafion, which was developed by DuPont Company as an ion-exchange resin in 1960's, is composed of a polytetrafluoroethylene backbone with perfluorinated ether side chains terminated by sulfonic acid groups as shown below,



$$\begin{array}{l} -[(CF_2\text{-}CF_2)_x\text{-}\underset{|}{C}F\text{-}CF_2]_y\text{-} \\ \qquad\qquad\qquad\quad O\text{-}[CF_2\text{-}\underset{|}{C}F\text{-}O]_z\text{-}CF_2\text{-}CF_2\text{-}SO_3H \\ \qquad\qquad\qquad\qquad\qquad\quad CF_3 \end{array}$$

In the case of Nafion 117, $x = 6$, $y \cong 1{,}000$, $z = 1$. The spin crossover complex film by using Nafion was prepared in the following way. The acid form of Nafion 117 was immersed in an aqueous solution of

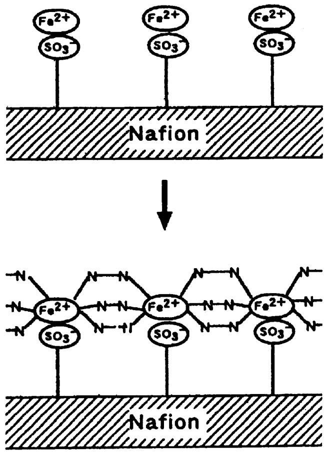


FIGURE 3. Synthetic process of $[Fe(Htrz)_3]$ film by using an ion-exchange film (Nafion).

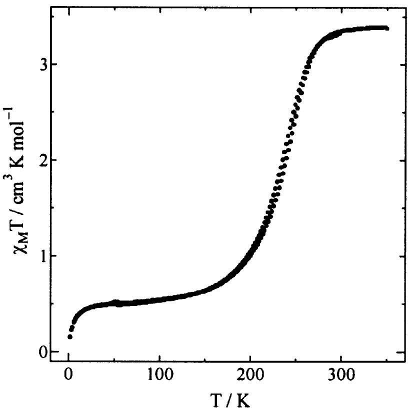


FIGURE 4. Temperature dependence of magnetic susceptibility for $[Fe(Htrz)_3]$ film.

$Fe(BF_4)_2$. After being immersed in the solution for 24 hours, the film was rinsed in methanol for an hour. After vacuum drying it at room temperature, the film was immersed in a methanol solution of Htrz for 24 hours. Then, the film was rinsed in methanol for an hour and stored with nitrogen gas. The preparation of spin crossover film is schematically shown in Fig. 3. The Nafion film treated in this way was colorless at room temperature. However, the color changed from transparent to purple with decreasing temperature, which implies the spin crossover phenomenon. Figure 4 shows the temperature dependence of the magnetic susceptibility of $[Fe(Htrz)_3]$ film. As shown in Fig. 4, the spin transition takes place at about 250 K.

Charge Transfer Phase Transition in $(C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$

In the case of mixed-valence complexes whose spin states lie in the spin-crossover region, new types of conjugated phenomena coupled with spin and charge are expected. From this viewpoint, we have synthesized the mixed valence complex, $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (dto = $C_2O_2S_2$), and have investigated the magnetic properties. $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ was synthesized in the following way. A solution of $KBa[Fe(dto)_3]\cdot 6H_2O$ in a methanol-water mixture was stirred. To this, a solution of $FeCl_2\cdot 4H_2O$ and $(n\text{-}C_nH_{2n+1})_4NBr$ in a methanol-water mixture were added. In this way, $(n\text{-}C_nH_{2n+1})_4N\ [Fe^{II}Fe^{III}(dto)_3]$ was obtained as black colored precipitate.

$(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ is presumed to have a two- or three-dimensional network structure with an alternating array of Fe^{III} and Fe^{II} ions through dto bridges, which is estimated by the structural analogy with $(Ph)_4P[Mn^{II}Cr^{III}(ox)_3]$[8]. Figure 5 shows the ^{57}Fe Mössbauer spectra of $(n\text{-}C_3H_7)_4N\ [Fe^{II}Fe^{III}(dto)_3]$ at 200 K and 77 K. At 200 K, the spectrum with two branches at 0.16 mm/s and 1.86 mm/s is assigned to that of Fe^{II} ion coordinated by six O atoms. The isomer shift and quadrupole splitting are quite similar to those of Fe^{II} in $(n\text{-}C_4H_9)_4N[Fe^{II}Fe^{III}(ox)_3]$[9]. The single peak at 0.48 mm/s is assigned to that of Fe^{III} ion coordinated by six S atoms. The isomer shift and quadrupole splitting are quite similar to those of $KBa\ [Fe^{III}(dto)_3]$[10].

As shown in Fig. 5, as temperature is decreased, the line profile of ^{57}Fe Mössbauer spectra remarkably changes around 120 K. At 77 K, the intensity of the spectrum corresponding to the Fe^{II} ion reduces down to 20 % and new lines at about 0.2 mm/s and 1.0 mm/s appear, which implies that the temperature induced charge transfer transition between the Fe^{II} and Fe^{III} sites takes place around 120 K. Comparing with the typical values of isomer shift (IS) and quadrupole splitting (QS) of ^{57}Fe Mössbauer spectra for $Fe^{II}(S= 0)$, $Fe^{II}(S= 2)$, $Fe^{III}(S= 1/2)$, and $Fe^{III}(S= 5/2)$, the ^{57}Fe Mössbauer spectra of $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ at 200 K and 77 K are assigned as shown in Fig. 5. In order to prove the charge transfer phase transition at 120 K, we have measured ESR spectra around 120 K. In the cases of the high-spin state (S= 2) of Fe^{II} and the low-spin state (S=1/2) of Fe^{III}, ESR signal can not be observed around

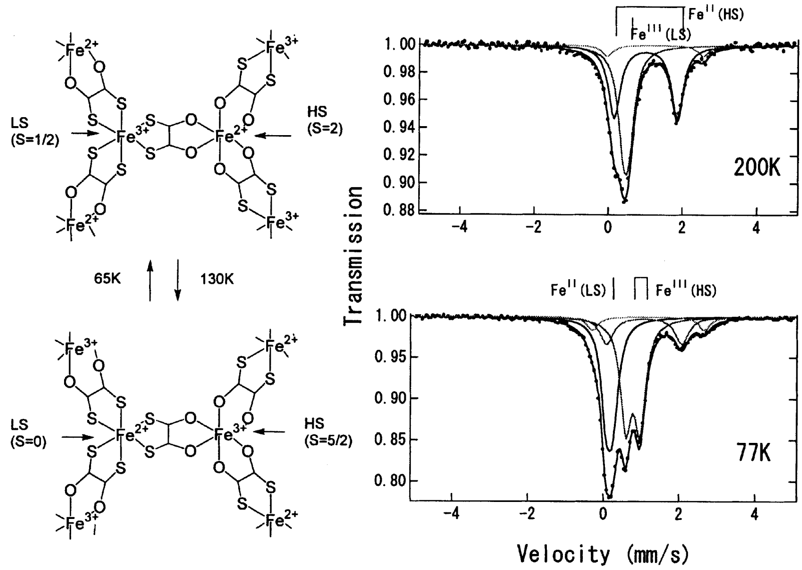


FIGURE 5. ^{57}Fe Mössbauer spectra and charge transfer phase transition of $(n\text{-}C_3H_7)_4N$ $[Fe^{II}Fe^{III}(dto)_3]$.

120 K because of rapid spin-lattice relaxation. ESR signal around 120 K is observable only for the high spin state (S= 5/2) of Fe^{III}. In fact, the ESR signal corresponding to Fe^{III} with S= 5/2 appears below 120 K, and its intensity becomes strong with decreasing temperature.

From the detailed analysis of ^{57}Fe Mössbauer spectra and ESR spectra around 120 K, it is concluded that $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ shows a reversible charge transfer phase transition at about 120 K, which is schematically shown in Fig. 5. In the higher temperature phase, the Fe^{III}(S=1/2) and Fe^{II}(S=2) ions are coordinated by six S atoms and six O atoms, respectively. In the lower temperature phase, on the other hand, the Fe^{III}(S=5/2) and Fe^{II}(S=0) ions are coordinated by six O atoms and six S atoms, respectively.

In the lower temperature phase of $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$, the ferromagnetic phase transition takes place at 6 K. The ferromagnetic order is presumably induced by the charge transfer interaction between the $Fe^{III}(S=5/2)$ and $Fe^{II}(S=0)$ ions.

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