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Control of T_C by isomerization of anion in Fe(II) spin-crossover complexes, [Fe(4-NH_2trz)$_3$](*o*-, *m*-, *p*-$NH_2C_6H_4SO_3$)$_2$·$2H_2O$

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Introduction

Fe(II) complexes coordinated by triazole are known to show a spin transition between the low-spin state (S=0) and the high-spin state (S=2) with a large thermal hysteresis around room temperature.[1,2] Such spin-crossover complexes are attracting much attention from a viewpoint of molecular devices. In this system, the spin-transition temperature T_C and the hysteresis width ΔT are controlled by not only ligand molecule but also anion. In the present work, we have investigated the effect of the structural isomerism of anion on T_C and ΔT in the title spin-crossover system. We measured magnetic properties and Fe *K*-edge EXAFS spectra. Single crystals have not been obtained for the title compounds.

Experimental

[Fe(4-NH_2trz)$_3$](*o*-, *m*-, *p*-$NH_2C_6H_4SO_3$)$_2$·$2H_2O$ was synthesized in the same way as reported in our previous paper.[3] Temperature dependence of magnetic susceptibility was measured by a Quantum Design MPMSXL SQUID susceptometer. Fe *K*-edge EXAFS spectra were taken in the conventional transmission mode at BL-10B in Photon Factory (operation energy of 2.5 GeV and stored current of 400-200 mA) in Institute of Materials Structure Science. A water-cooled Si(311) channel-cut crystal was employed as a monochromator. Samples were diluted with BN to give a pellet. In order to avoid the loss of crystal water in vacuum, the pellet was completely sealed with an adhesive substrate (Stycast No.1266).

Results and Discussion

Fe *K*-edge EXAFS spectra of the compounds were investigated. Figure1 shows the Fourier transforms of each spectrum at 30K, where Fe(II) irons are in the low-spin state. The main peak at about 1.6Å corresponds to the Fe-N scattering. The peak around 7 Å corresponding to the Fe-Fe-Fe multiple scattering proves the existence of linear Fe chain structure in [Fe(4-NH_2trz)$_3$](*o*-, *m*-, *p*-$NH_2C_6H_4SO_3$)$_2$·$2H_2O$. The detailed analysis using FEFF theoretical model is in progress.

Temperature dependence of the magnetic susceptibility of [Fe(4-NH_2trz)$_3$](*o*-, *m*-, *p*-$NH_2C_6H_4SO_3$)$_2$·$2H_2O$ is shown in Figure2. In the case of *o*-salt, with increasing temperature, an abrupt spin transition occurs at T_C(up)=341K. In the cooling process, the spin transition with ΔT=9K occurs abruptly at T_C(down)=332K.

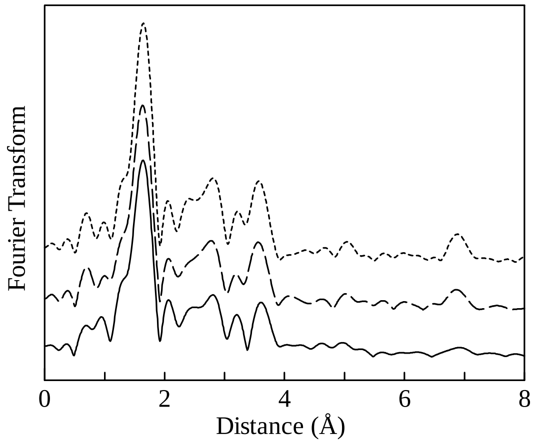

Fig.1 Fourier transforms of EXAFS spectra for [Fe(4-NH_2trz)$_3$](*o*-, *m*-, *p*-$NH_2C_6H_4SO_3$)$_2$·$2H_2O$ at 30K. Solid line: *p*-salt, dashed line: *m*-salt, dotted line: *o*-salt.

In the case of *m*-salt, T_C(up)=331K and T_C(down)=305K were obtained with ΔT=26K. In the case of *p*-salt, with increasing temperature, the spin transition occurs stepwise around 240K and 310K. In the cooling process, the spin transition occurs also stepwise around 290K and 230K. The two-step spin transition would be attributed to non-equivalent lattice site of Fe(II).

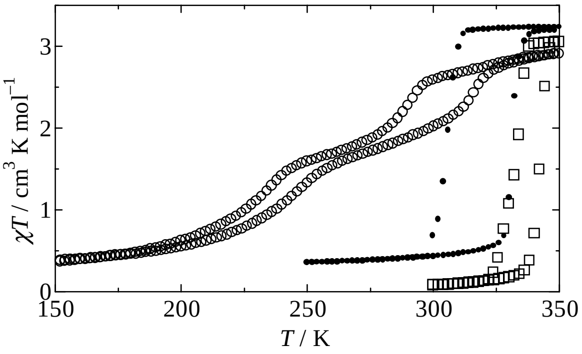

Fig.2 χT versus T plot of [Fe(4-NH_2trz)$_3$](*o*-, *m*-, *p*-$NH_2C_6H_4SO_3$)$_2$·$2H_2O$. Square: *o*-salt, dot: *m*-salt, circle: *p*-salt.

References

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