Study on static and dynamic spin-crossover tripyrazolylmethane iron(II) complexes by using μSR spectroscopy

N. Kojima,[*1] H. Kobayashi,[*1] A. Okazawa,[*1] I. Kawasaki,[*2] and I. Watanabe[*2]

Transition-metal complexes have attracted much attention from the viewpoints of magnetic, redox, and optical properties originating from *d* spins. In particular, complexes with a d^4–d^7 configuration have the possibility of undergoing spin crossover transitions between low-spin (LS) and high-spin (HS) states, showing bistability with color and magnetic susceptibility changes. Spin-crossover phenomena can be classified into two types according to the time window of a measurement, (i) static spin crossover, which is often observed with a thermal hysteresis, and (ii) dynamic spin crossover, which sometimes shows an equilibrium obeying the van't Hoff equation (i.e., spin equilibrium).

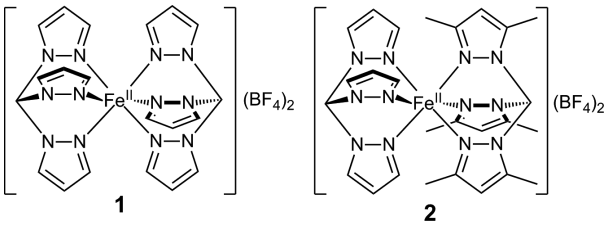
A large number of spin-crossover iron(II) complexes have been developed and their spin dynamics has been investigated by means of Mössbauer spectroscopy, nuclear magnetic resonance, neutron scattering, etc. Muon spin relaxation (μSR) spectroscopy, which has the unique time range (10^{-5} ~ 10^{-11} s) to observe magnetic fluctuations, is useful for the investigation of spin-crossover phenomena. However, the μSR spectroscopy has scarcely been applied to the study of dynamic spin-crossover systems. To investigate the rapid spin equilibrium in detail, we selected iron(II) complexes containing tripyrazolylmethane ligands (Fig. 1), $[Fe\{(pz)_3CH\}_2](BF_4)_2$ (**1**; pz = 1-pyrazolyl) and $[Fe\{(pz)_3CH\}\{(3,5\text{-}Me_2pz)_3CH\}](BF_4)_2$ (**2**), which show dynamic and static spin crossover, respectively, on ^{57}Fe Mössbauer spectroscopy.[1,2] Similar molecular structures of **1** and **2** facilitate μSR study. Thus, we can expect that positive muons would be trapped at the same sites in their compounds.

Polycrystalline samples of **1** and **2** were wrapped in silver foil and stuck to a silver plate. We used He-flow cryostats in the temperature range between 50 and 475 K for **1** and between 50 and 300 K for **2**. μSR time spectra were obtained in the zero field (ZF) and longitudinal field (LF) applied along the direction of the initial muon-spin polarization. LF-μSR spectra were analyzed using eq (1):

$$A(t) = a_f\exp(-\lambda_f t) + a_s\exp(-\lambda_s t) + a_{bg}, \quad (1)$$

where a_f and a_s are initial asymmetries, λ_f and λ_s are the muon-spin relaxation rates for the fast and slow relaxation components, respectively. For ZF-μSR, we analyzed the spectra considering a single relaxation process ($a_s = 0$).

The LF-μSR spectra of both **1** and **2** show a similar tendency. In the spectra at 100 K corresponding to LS states, fast relaxations were observed for **1** and **2**, which were decoupled by a field of 1000 Oe. The behavior indicates the formation of paramagnetic muonium species in pyrazolyl rings. The fluctuation can be completely decoupled at 3000 Oe.



1 2

Fig. 1. Structural formula of $[Fe\{(pz)_3CH\}_2](BF_4)_2$ (**1**) and $[Fe\{(pz)_3CH\}\{(3,5\text{-}Me_2pz)_3CH\}](BF_4)_2$ (**2**).

On the other hand, the initial asymmetry in the HS states (**1**: 475 K; **2**: 300 K) is lower, even above 1000 Oe, compared to those in the LS states, suggesting the existence of other strong fluctuations. The time spectra of **1** and **2** in LF = 3000 Oe drastically changed with a change of temperature, and the relaxation rates (λ_f) derived from strong fluctuations increased on heating. We found that the temperature dependences of λ_f strongly correlate with $\chi_{mol}T$ vs T profiles (Fig. 2). Thus, the results clarified that μSR spectroscopy using a high LF can detect spin transitions in both dynamic and static spin-crossover complexes.

In the ZF-μSR spectra, there is an apparent difference between temperature dependences of the initial asymmetries of **1** and **2**. The initial asymmetry of **1** decreased around the spin transition, although that of **2** was constant over the entire temperature range. Such a decay is presumably caused by the spin fluctuation of the equilibrium between the HS and LS. The detailed analysis is now in progress.

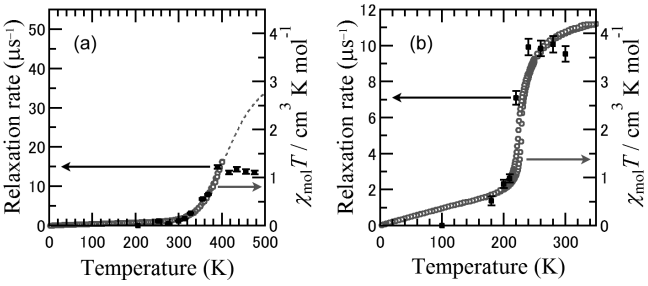


Fig. 2. Temperature dependences of relaxation rates (λ_f) under LF = 3000 Oe for (a) **1** and (b) **2**. The λ_f plots are superimposed on $\chi_{mol}T$ vs T plots.

References

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2) B. Moubaraki et al.: Dalton Trans. 4413 (2007).

*1 Graduate School of Arts and Sciences, The University of Tokyo
*2 RIKEN Nishina Center