MLF Experimental Report	提出日 Date of Report Jan. 13, 2013
課題番号 Project No. 2012A0067 実験課題名 Title of experiment Muon spin researches of valence-trapping and detrapping in mixed-valence trinuclear carboxylate iron complexes 実験責任者名 Name of principal investigator Yoichi Sakai 所属 Affiliation: Daido University	装置責任者 Name of responsible person Yasuhiro Miyake 装置名 Name of Instrument/（BL No.） D1 実施日 Date of Experiment Oct. 24-26, 2012

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Name:

Mixed-valence trinuclear iron pentafluorobenzoate complex with dichloromethane as crystalline solvent

Chemical form:

$Fe_3O(C_6F_5COO)_6(C_5H_5N)_3{\cdot}CH_2Cl_2$ (“Fe_3” is “$Fe^{3+}Fe^{3+}Fe^{2+}$” or “$Fe^{2.7+}{}_3$”.)

Physical state:

Polycrystalline powder

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

The sample $Fe_3O(C_6F_5COO)_6(C_5H_5N)_3{\cdot}CH_2Cl_2$ in the present experiment was prepared by us as a novel compound.

The molecular structure of mixed-valence trinuclear metal carboxylate complex, $M_3O(R\text{-}COO)_6L_3$ is shown in Figure 1, where L is a ligand such as pyridine. The three largest circles are Fe^{3+} (gray-colored) or Fe^{2+} (white) ions. Small gray- and black-circles represent C and O atoms, respectively. R is a pentafluoro-phenyl group, $-C_6F_5$. The dotted lines represent the coordination bonds. It is shown from our recent Mössbauer study of this mixed-valence complex that the iron-valence fluctuating rate should be faster than the Mössbauer time scale of 140 ns, leading to an average valence of $Fe^{2.7+}$ at room temperature .[1]

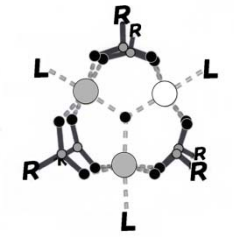
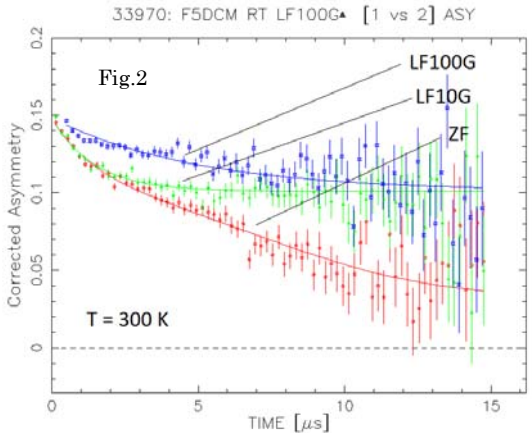


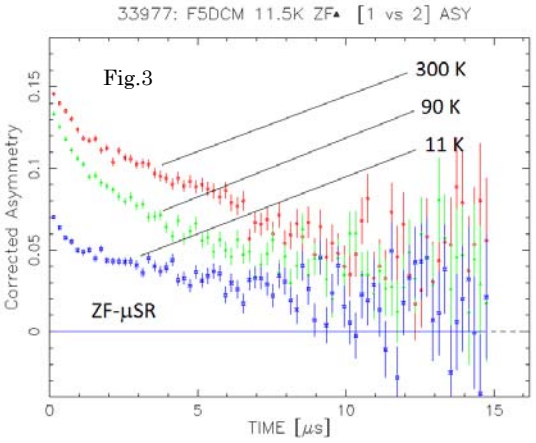
Figure 1

Our present experiment was carried out at the MUSE D1 area of MLF/J-parc in order to probe the valence-fluctuation of tri-iron in the complex using positive muon spin research (μSR) methods.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Relaxation of positive muon spin polarization was measured for $Fe_3O(C_6F_5COO)_6(C_5H_5N)_3 \cdot CH_2Cl_2$ over the temperature range of 11 k to 300 K, under a zero magnetic field (ZF) and longitudinal magnetic fields (LF). In Figures 2 and 3 are shown the muon spin relaxation curves, the upper (Fig.2) of which are for those at 300 K under LFs of 100, 10 G, and a ZF. The lower (Fig.3) is for those under a ZF over a wide temperature range from 11 K to 300 K.





Figures 2 and 3 : Time-spectra of positive muon spin relaxation of $Fe_3O(C_6F_5COO)_6(C_5H_5N)_3 \cdot -CH_2Cl_2$. (upper=Fig.2) at 300 K, under LFs of 100 G, 10 G, and a ZF. (lower=Fig.3) under a ZF, over a temperture range from 11 K to 300 K .

In Figure 2, the following findings were shown;

1) Under a ZF at 300 K, spin polarization, proportional to "Asymmetry" of the ordinate, was observed to relax (decrease) swiftly.
2) Under a LF of 10 G, about two thirds of muons recovered the spin-polarization, which might be due to decoupling-effect between muon spins and static nuclear magnetic moments with a random direction.
3) One third of muon-spins relaxed under LF 10 G was partially (or incompletely) decoupled under LF 100 G, tentatively being ascribable to the muon component depolarized through the magnetic interaction with the fluctuating electronic spin of the $Fe_3O(C_6F_5COO)_6 -(C_5H_5N)_3 \cdot CH_2Cl_2$ under a ZF or LF 10 G. The correlation time of muon spin decoupled under LF 100 G should be estimated 120 ns, approximately close to the lifetime (140 ns) of the Mössbauer excited nuclear level in ^{57}Fe, i.e., the time constant of the electronic fluctuation of the mixed-valence.

It might be concluded in the present work that we have observed the electronic fluctuation, resulting in the valence detrapping in the mixed-valence complex, by μSR for the first time, although further experiments and discussions should be needed. The implication of the results shown in Figure 3 is under consideration now.

[1]. Y. Sakai et al. *Hyperfine Interactions*, 205, 1-5 (2012)