

# Mössbauer spectroscopic study on valence-detrapping and trapping of mixed-valence trinuclear iron(III, III, II) fluorine-substituted benzoate complexes

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**Abstract** Four mixed-valence trinuclear iron(III, III, II) fluorine-substituted benzoate complexes were synthesized;  $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$  (**1**),  $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  (**2**),  $\text{Fe}_3\text{O}(\text{2H-C}_6\text{F}_4\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  (**3**), and  $\text{Fe}_3\text{O}(\text{4H-C}_6\text{F}_4\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  (**4**), in which valence-detrapping and trapping phenomena have been investigated by  $^{57}\text{Fe}$ - Mössbauer spectroscopy. The valence state of the three iron ions is trapped at lower temperatures while it is fully detrapped at higher temperatures for **1**. Valence detrapping is not observed for **2**, **3**, and **4** even at room temperature, although Mössbauer spectra for **3** and **4** show complicated temperature dependence.

**Keywords**  $^{57}\text{Fe}$ -Mössbauer spectroscopy · Valence-detrapping and trapping · Mixed-valence trinuclear iron fluorine-substituted benzoate complexes

## 1 Introduction

Mixed-valence trinuclear iron(III, III, II) carboxylate complexes have attracted intensive attention from many chemists in the field of Mössbauer spectroscopy, where two  $\text{Fe}^{3+}$  ions and one  $\text{Fe}^{2+}$  ion exist in three chemically similar sites in the crystal. The extent of such site similarity being dependent on various conditions, it is a subtle and interesting problem whether the valence states of the

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three iron ions are in a detrapped (averaged) state or in a trapped state. Although many Mössbauer studies have been reported so far for such trinuclear iron carboxylates, only few papers have been published for benzoate complexes and benzoate-derivatives probably because of synthetic difficulties. In 2003, mixed-valence  $\text{Mn}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$  was synthesized and single crystal ESR spectra were analyzed on the basis of X-ray structure analysis by Ito et al. [1]. We have succeeded in the synthesis of the mixed-valence trinuclear iron(III, III, II) fluorine-substituted benzoate by a similar method, and studied the valence states of iron ions by the Mössbauer technique.

## 2 Experimental

### 2.1 Materials

Four mixed valence trinuclear iron pentafluorobenzoate or tetrafluorobenzoate complexes were synthesized for the first time. The new products were identified by elemental analysis, TG-MS, FTIR spectroscopy, and Mössbauer spectroscopy.

**$\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$  (1)**  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in ethanol. To this was added an excess amount of pyridine and the mixture was stirred for 30 min.  $\text{C}_6\text{F}_5\text{COONa}$  (prepared with pentafluorobenzoic acid and sodium hydroxide) was added and the mixture was stirred for a few hours. The resulting precipitates were collected and subsequently dissolved in dichloromethane. After adding ethanol and hexane, the mixture was stored in a refrigerator for several days to afford dark-brown needle-like crystals (yield 30.0%) to grow.

Anal. Calcd (%) for  $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$ : C, 39.31; Cl, 4.00; F, 32.16; H, 0.97; N, 2.37. Found (%): C, 39.81; Cl, 3.09; F, 32.41; H, 1.04; N, 2.43.

IR (Nujol,  $\text{cm}^{-1}$ , selected):  $\nu(\text{OCO})_{\text{asym}}$ ; 1654 (s), 1637 (m), and 1608 (w).

A satisfactory analytical result for the Cl content has not yet obtained. However, TG-MS results for complex **1** showed that the ratio of  $\text{Fe}_3\text{O}$  cluster/solvate molecule  $\text{CH}_2\text{Cl}_2$  is close to 1.0. The ratio has been also confirmed by our preliminary single-crystal X-ray structural determination, which will be reported elsewhere soon.

**$\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  (2)** Polycrystalline solvate complex **1** was heated for 2 hours at  $135^\circ\text{C}$  under a reduced pressure of 0.1 Torr, to remove solvate  $\text{CH}_2\text{Cl}_2$ , on the basis of our TG-MS data for **1**.

Anal. Calcd (%) for  $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$ : C, 40.57; F, 33.78; H, 0.90; N, 2.49. Found(%): C, 39.66; F, 34.11; H, 0.92; N, 2.17.

IR (Nujol,  $\text{cm}^{-1}$ , selected):  $\nu(\text{OCO})_{\text{asym}}$ ; 1654 (m), 1637 (m), and 1605 (w).

The elemental analysis suggested that there might be a little thermal decomposition.

**$\text{Fe}_3\text{O}(\text{2H}-\text{C}_6\text{F}_4\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  (3) and  $\text{Fe}_3\text{O}(\text{4H}-\text{C}_6\text{F}_4\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  (4)** These two complexes were synthesized by a similar method to that of **1** described above, using sodium 2,3,4,5-tetrafluorobenzoate and sodium 2,3,5,6-tetrafluorobenzoate, and the yield was 25.0 and 36.6% for **3** and **4**, respectively.

Anal. Calcd (%) for  $Fe_3O(2H-C_6F_4COO)_6(C_5H_5N)_3$ : C, 43.35; F, 28.87; H, 1.34; N, 2.65. Found (%): C, 43.27; F, 28.87; H, 1.44; N, 2.63.

IR (Nujol,  $cm^{-1}$ , selected):  $\nu(OCO)_{asym}$ ; 1652 (m), 1636 (m), and 1604 (w).

Anal. Calcd (%) for  $Fe_3O(4H-C_6F_4COO)_6(C_5H_5N)_3$ : C, 43.35; F, 28.87; H, 1.34; N, 2.65. Found (%): C, 42.72; F, 28.71; H, 1.39; N, 2.69.

IR (Nujol,  $cm^{-1}$ , selected):  $\nu(OCO)_{asym}$ ; 1637 (s), and 1605 (m).

## 2.2 $^{57}Fe$ -Mössbauer measurements

Mössbauer measurements were performed in an ordinary mode with a Mössbauer spectrometer with a  $^{57}Co(Rh)$  source. The measurement temperature was ranged from 5 K to 300 K. The spectral curve fitting was carried out by using MossWinn 4.0Pre software. The isomer shift and Doppler velocity scale were calibrated with respect to metallic iron at room temperature.

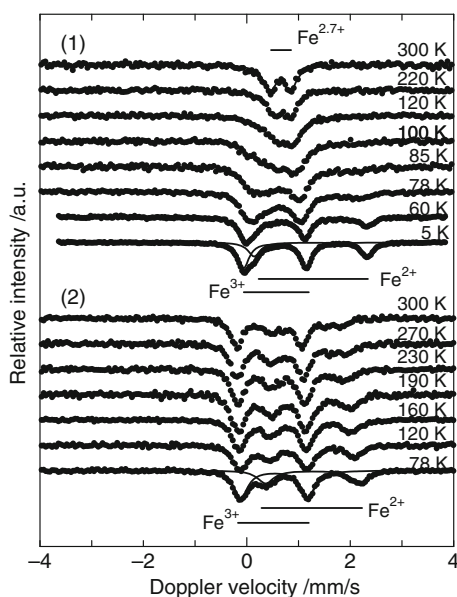
## 3 Results and discussion

The temperature-dependent Mössbauer spectra are shown in Figs. 1 and 2 for trinuclear iron pentafluorobenzoate complexes (**1** and **2**) and tetrafluorobenzoate complexes (**3** and **4**), respectively.

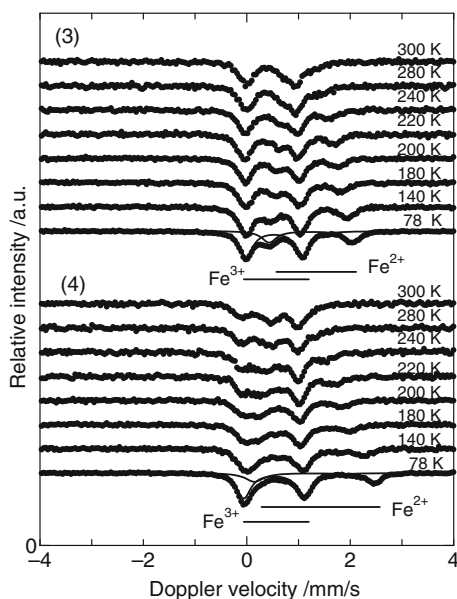
As shown in the upper part of Fig. 1, the spectral line-shapes of **1**, which contains  $CH_2Cl_2$  as a solvate molecule in the crystalline solid, are quite sensitive to temperature. Two pairs of the absorption doublet are separately observed with an area ratio of about 2:1 at 5 K. The isomer shift and the quadrupole splitting are estimated as follows: 0.54 mm/s and 1.21 mm/s for the higher intense doublet, and 1.23 mm/s and 2.19 mm/s for the lower one. The intensity ratio and Mössbauer parameters reveal that the valence state of the three iron ions should be trapped in two  $Fe^{3+}$  and one  $Fe^{2+}$ . Only one doublet was observed at 300 K with an isomer shift of 0.64 mm/s and a quadrupole splitting of 0.40 mm/s, implying that all iron ions should be in a fully detrapped valence state of +2.7, calculated as  $[(+3) \times 2 + (+2)]/3 = 2.7$ . Unfortunately it has not yet been successful to decompose the possible components at transient temperatures in the present analysis because of the complicated line-shapes. However, it is possible to estimate the transition temperature from the trapped to the detrapped state, ranging from 70 K to 100 K.

Complex **2** does not show an essential transformation from the trapped iron valence type to the detrapped type judging from the temperature dependence of the Mössbauer spectral line-shapes (the lower part of Fig. 1). This indicates that the valence-trapped state survives over the whole temperature range scanned in the present work. Hendrickson's group reported for the first time that the Mössbauer spectra of the mixed-valence trinuclear iron acetate complex at room temperature showed the detrapped type when it possessed one or more solvate molecules,  $Fe_3O(CH_3COO)_6(C_5H_5N)_3 \cdot C_5H_5N$ , while the trapped type spectra were observed upon the loss of solvate molecules at room temperature [2, 3]. Sorai's group have interpreted such phenomena from their molecular thermodynamic experiments and theoretical considerations [4]; they demonstrated that the phase transition of the mixed-valence complex should be associated with the intramolecular electron-transfer leading to valence detrapping, the rate of which might be accelerated by the

**Fig. 1** Temperature dependence of  $^{57}\text{Fe}$ -Mössbauer spectra of  $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$  **1** and  $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  **2**



**Fig. 2** Temperature dependence of  $^{57}\text{Fe}$ -Mössbauer spectra of  $\text{Fe}_3\text{O}(2\text{H}-\text{C}_6\text{F}_4\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  **3** and  $\text{Fe}_3\text{O}(4\text{H}-\text{C}_6\text{F}_4\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$  **4**



presence of solvate molecules in the crystalline state. The mechanism was proven in terms of an unusually large transition entropy estimated from the heat capacity data, being due to a number of the rotational orientations of solvate molecules immediately after the transformation.

The variable-temperature Mössbauer spectra for **3** and **4** are exhibited in the upper part and the lower part of Fig. 2, respectively. The spectral-line shapes depend

significantly on the temperature for both complexes. The isomer shift is evaluated to be 0.46 mm/s by curve fitting of the spectrum at 300 K for **3** assuming one doublet although a little asymmetry is being observed. This value is not close to the isomer shift value ranging 0.65 to 0.75 mm/s at room temperature for the tri-iron carboxylate complexes in a fully valence-detrapped state [3, 5, 6], and also far from that (0.64 mm/s) for **1** described above. The spectra should rather be considered to be trapped one. As shown in Fig. 2, only a small change is observed in the peak positions of the doublet for the  $\text{Fe}^{3+}$  component while those for  $\text{Fe}^{2+}$  move to a much higher extent. Similar temperature dependence was reported for mixed-valence  $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-CH}_3\text{-C}_5\text{H}_4\text{N})_3\cdot\text{CH}_3\text{CN}$  by Oh et al. [5]; they explained that the quadrupole splitting of  $\text{Fe}^{2+}$  decreased greatly with the rise of temperature, because the electron population of each 3d-orbital in the low-lying electronic states ( $t_{2g}$ ) becomes close by thermal activation, which results in a decrease of the electric field gradient by the valence electrons, for some high-spin  $\text{Fe}^{2+}$  compounds such as binuclear iron complexes of the binucleating clathrochelate ligand [7] and  $\text{Fe}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$  [8]. The quadrupole splitting for octahedral high-spin  $\text{Fe}^{3+}$  species with five 3d electrons is not expected to vary with the increase of temperature, because five electrons are equally populated in the five orbitals ( $e_g$ )<sup>2</sup>( $t_{2g}$ )<sup>3</sup>. We are tempted to interpret our observations that the Mössbauer spectral line shapes vary in a complicated manner with temperature for **3** and **4** in terms of the aforementioned mechanisms. Therefore, we conclude at this moment that the valence of three iron ions should be trapped even at 300 K for **3** and **4**.

## References

1. Ito, M., et al.: *Inorg. Chim. Acta.* **353**, 51 (2003)
2. Oh, S.M., et al.: *J. Am. Chem. Soc.* **106**, 7984 (1984)
3. Woehler, S.E., et al.: *J. Am. Chem. Soc.* **109**, 1063 (1987)
4. Sorai, M., et al.: *J. Am. Chem. Soc.* **108**, 702 (1986)
5. Oh, S.M., et al.: *J. Am. Chem. Soc.* **109**, 1073 (1987)
6. Nakamoto, T., et al.: *Inorg. Chem.* **36**, 4347 (1997)
7. Temken, M.D., et al.: *Inorg. Chem.* **24**, 4202 (1985)
8. Merrithew, P.B., et al.: *Inorg. Chem.* **10**, 1401 (1971)