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Notes

Mössbauer Study on the Electron Transfer Rate Depending on the Intermolecular Interaction in Iron(II, III) Mixed-Valence Complex

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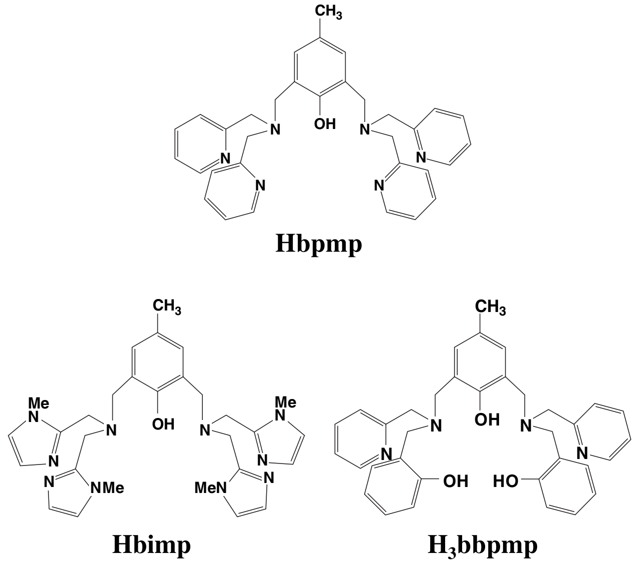
^{57}Fe Mössbauer spectroscopy has revealed that carboxylato bridged binuclear iron complex, $[Fe^{II}Fe^{III}(bpmp)(ena)_2](ClO_4)_2$, exhibits a mixed-valence state depending on temperature, where bpmp = 2,6-bis[bis-(2-pyridylmethyl)-aminomethyl]-4-methylphenol and Hena = enanthic acid. Both of the polycrystalline sample and the film sample prepared by dispersing the complex in poly(methyl methacrylate) (PMMA) have been investigated. The rate of the intramolecular electron transfer between iron(II) and iron(III) ions for the polycrystalline sample abruptly increases above ca. 200 K, and that for the film sample is slightly increase in the temperature range of 80 K to 295 K. The results show that the intermolecular interactions affect the intramolecular electron transfer of the binuclear mixed-valence iron complex.

It is well known that mixed-valence iron clusters of the active sites of metalloproteins play important roles in biological systems.[1] The model compounds of these compounds have been studied intensively and characterized by using various methods. One of the model complexes is a family of carboxylato mixed-valence diiron(II,III) complexes. For example, mixed-valence diiron complexes with a heptadentate polypyridine ligand (bpmp),[2] the ligand having imidazol groups (bimp),[3] and the ligand having phenol groups (bbpmp),[4] have been reported previously (scheme 1).

In the investigation of mixed-valence complexes with such ligands, knowledge of the mechanism of the electron transfer between the two iron centers is most important. Furthermore, in the field of nanomaterial science, understanding the electron transfer phenomena at single molecule level is also important. The mixed-valence diiron(II,III) bpmp complexes with various carboxylic acid were reported by Maeda et al. previously, and characterized by using Mössbauer spectroscopy.[5] They reported that the electron trapped/detrapped states are affected by the kind of carboxylic acids, being bridging ligands. They also suggested that the rate of the intramolecular electron transfer is influenced by the crystal packings. Therefore it is thought that the intermolecular interactions play an important role in the electron transfer of the mixed-valence state.



Hbpmp

Hbimp

H$_3$bbpmp

Scheme 1. Structures of the ligands.

We focused on the intermolecular interactions in the mixed-valence state, and prepared two types of samples of the mixed-valence diiron(II,III) compound $[Fe^{II}Fe^{III}(bpmp)(ena)_2](ClO_4)_2$, where Hbpmp represents 2,6-bis[bis-(2-pyridylmethyl)-aminomethyl]-4-methylphenol and Hena represents enanthic acid (Figure 1). One is a polycrystalline sample as prepared and the other is a film sample.[6,7] The film sample was prepared by mixing an acetonitrile solution of poly(methyl methacrylate) (PMMA) and an acetonitrile solution of the complex, and obtained as a transparent film.[8] In the film sample, the complex molecules were dispersed completely at a single molecular level and thus the intermolecular interaction would be very weak.

Herein, we report that the rates of the electron transfer for the polycrystalline and film samples are different, depending on the strengths of the intermolecular interactions. Hereafter, the polycrystalline sample of $[Fe^{II}Fe^{III}(bpmp)(ena)_2](ClO_4)_2$ is represented as **1**, and the film sample as **2**.

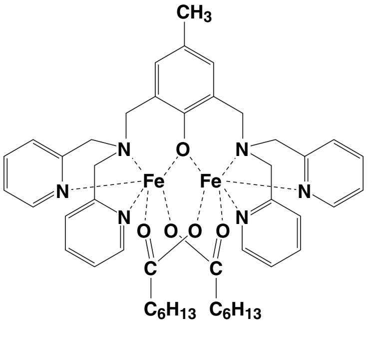


Figure 1. Chemical structure of $[Fe_2(bpmp)(ena)_2]^{2+}$.

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The temperature dependences of the Mössbauer spectra of **1** and **2** were measured.[9] The Mössbauer spectra of **1** and **2** are shown in Figures 2(a) and (b). The Mössbauer spectrum of **1** shows an asymmetric doublet at 295 K, *Q.S.* (quadrupole splitting) = 0.76 mm s^{-1} and *I.S.* (isomer shift) = 0.96 mm s^{-1}, assigned to delocalized valence states for iron(II) and iron(III) species. The delocalized valence states were observed above 220 K. This indicates that the rate of the electron transfer between iron(II) and iron(III) atoms becomes comparable to the Mössbauer hyperfine frequency. On the other hand, the spectrum at 80 K of **1** shows two doublets; one is of iron(II) high-spin species with *Q.S.* = 2.80 mm s^{-1} and *I.S.* = 1.17 mm s^{-1}, the other is of iron(III) high-spin species with *Q.S.* = 0.55 mm s^{-1} and *I.S.* = 0.55 mm s^{-1}. Two doublets were observed below 220 K, and the area ratio of iron(II) : iron(III) species is 1 : 1. Temperature dependence of Mössbauer spectra of **2** was different from that of **1**. In the spectra of **2**, two doublets were observed at 295 K. The parameters are *Q.S.* = 1.61 mm s^{-1} and *I.S.* = 0.90 mm s^{-1} for the iron(II) high-spin species, and *Q.S.* = 0.50 mm s^{-1} and *I.S.* = 0.41 mm s^{-1} for the iron(III) high-spin species at 295 K. At 80 K, the spectrum of **2** also shows two doublets; one is of iron(II) high-spin species with *Q.S.* = 2.52 mm s^{-1} and *I.S.* = 1.19 mm s^{-1}, the other is of iron(III) high-spin species with *Q.S.* = 0.53 mm s^{-1} and *I.S.* = 0.53 mm s^{-1}. The values of the parameters are similar to those of **1** at 80 K. The area ratio of iron(II) : iron(III) species in **2** is 1 : 1, which indicates that no further oxidation of iron(II) ions occurred while preparing the film. For **2**, two doublets of iron(II) and iron(III) species were observed in the temperature range of 80 – 295 K. At 80 K, the line width of Mössbauer spectra of **1** is 0.41 mm s^{-1} for iron(II) species and 0.47 mm s^{-1} for iron(III) species. On the other hand, that of **2** is 0.63 mm s^{-1} for iron(II) and 0.58 mm s^{-1} for iron(III) species. The line widths of the Mössbauer spectra of **2** are broader than those of **1**. In the film sample, it is thought that the molecules exist in the similar structure to the solution sample, and the distorted environment around central metals introduced in PMMA matrix may cause the broad line width.

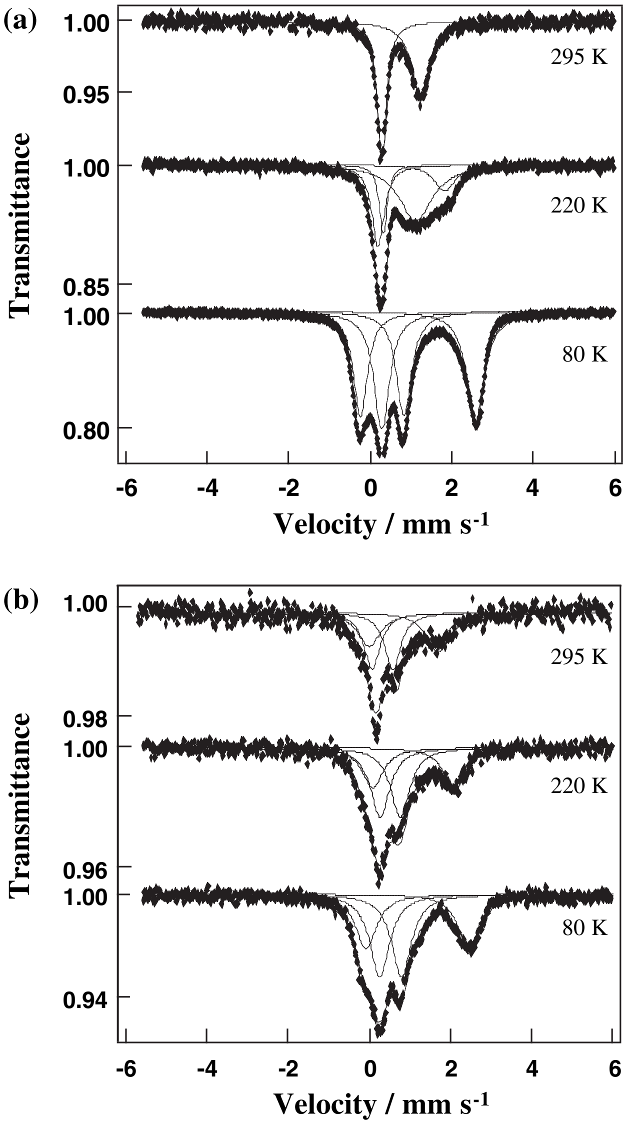

Figure 2. Temperature dependence of the Mössbauer spectra of **1** (a) and **2** (b).

Furthermore, the rate of electron transfer between iron(II) and iron(III) ions can be estimated by fitting the Mössbauer spectra of **1** and **2** using the method of Wickmann.[10] To estimate the relaxation time τ and the rate of electron transfer λ, the fitting analysis was carried out by the following equations,

$$\tau = \frac{\tau_1 \tau_2}{\tau_1 + \tau_2}, \tag{1}$$

$$\lambda = \frac{1}{\tau}, \tag{2}$$

where τ_1 and τ_2 are the electron relaxation time of each transition for iron(II) and iron(III) ions. The temperature dependence of λ for **1** and **2** are shown in Figure 3. The value of the rate is almost constant (6.3×10^5 s^{-1}) below ca. 140 K for **1**. On heating, the value exponentially increases from 8.8×10^5 s^{-1} at 200 K to 3.6×10^7 s^{-1} at 295 K. On the other hand, the rate slightly increases from 1.6×10^6 at 80 K to 3.0×10^6 s^{-1} at 295 K for **2**. The rate of the intramolecular electron transfer for **1** is almost the same as that for **2** below 200 K. The rate for **1** is much faster than that for **2** at 295 K. The results for **2** show that the rate is hardly dependent on the temperature in the single molecule. Since the intermolecular interaction is weak enough in the film sample, and the intermolecular interactions would affect the intramolecular electron transfer in the binuclear mixed-valence iron complex.

In conclusion, we prepared the polycrystalline sample **1** and the film sample **2** of the binuclear iron complex, $[Fe^{II}Fe^{III}(bpmp)(ena)_2](ClO_4)_2$, and observed the different temperature dependence of the intramolecular electron transfer rate between **1** and **2** by using Mössbauer spectroscopy. The polycrystalline sample exhibited trapped-valence state below 140 K and detrapped-valence state above 200 K in the Mössbauer spectra. On the other hand, the film sample exhibited the trapped-

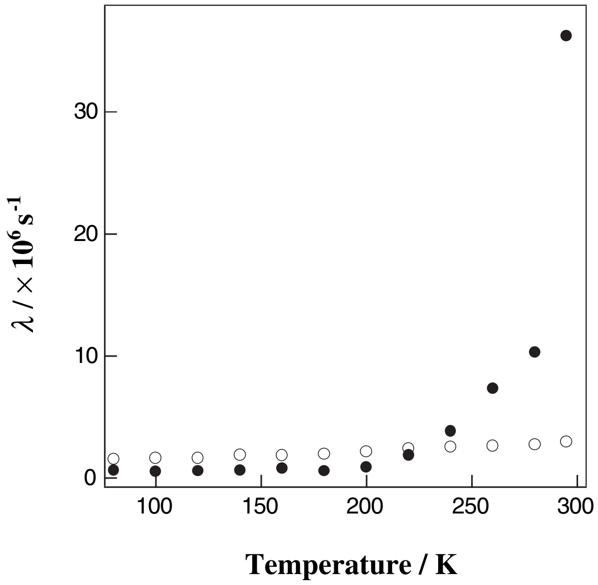

Figure 3. λ vs. *T* plots for **1** and **2**. Full plots (●) for **1** and open plots (○) for **2**.

valence state in the temperature range of 80 – 295 K. The results suggest that the intermolecular interaction greatly influences the electron transfer in the mixed-valence diiron(II,III) complex. The investigation of the electron transfer in single molecules will play important roles in the field of the nanomaterial science in the future.

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(7) The polycrystalline sample was prepared as reported previously.[6] *Anal.* Calcd. For $C_{51}H_{51}N_6Fe_2O_{13}Cl_2$: C, 55.02; H, 4.62; N, 7.38; Fe, 9.81. Found: C, 53.25; H, 4.54; N, 7.46; Fe, 9.57.

(8) A solution of PMMA (0.10 g) in acetonitrile (20 mL) was added to a solution of the complex (0.022 g, 20 mmol) in acetonitrile (20 mL). The mixture was stirred for 15 minutes and spread into schale. Dark-green films were collected after leaving one night.

(9) All isomer shifts are given relative to α-Fe at room temperature.

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