1. Introduction

A number of $^{57}$Fe-Mössbauer spectroscopic investigations of mixed-valence trinuclear iron carboxylate cluster complexes with a triangle array of iron cations ($\text{Fe}^{1+}, \text{Fe}^{2+}, \text{Fe}^{3+}$) have been intensively carried out by many researchers; the general chemical formula is $\text{Fe}_3\text{O}($R-COO$)_6L_3\cdot nS$, where R-COO$^-$ is a carboxylate anion, L, a ligand, and S, a crystalline solvated molecule ($n = 0, 1, 2, 3, \ldots$). The cluster molecular structure is depicted in Figure 1. In such cluster complexes, much intensive attention has been paid to the valence-detrapping (valence-averaging) through the electronic interactions among three iron cations. The first pioneering observation of valence-detrapping by $^{57}$Fe-Mössbauer spectroscopy was reported in 1984 by Hendrickson's group, who revealed that one set of quadrupole doublet ascribing to the detrapping valence of Fe$^{2.7+}$ was measured in $\text{Fe}_3\text{O}($CH$_3$COO$)_6($C$_5$H$_5$N$)_3\cdot$C$_5$H$_5$N at room temperature, while two separate sets of doublet due to Fe$^{3+}$ and Fe$^{2+}$ in a valence-trapped state below 100 K.

After that, a lot of trinuclear iron carboxylate complexes have been so far studied using Mössbauer techniques and there have been many interesting articles, most of which were about the valence-detrapping phenomena among three iron cations. As a rare case, Sato et al. reported that valence-detrappping between one Fe$^{3+}$ and one Fe$^{2+}$ was observed at higher temperature for $\text{Fe}_3\text{O}($CH$_2$ClCOO$)_6($H$_2$O$)_3\cdot$3H$_2$O. This partial valence-detrapping, in which one of two Fe$^{3+}$ ions participates, was explained from the sites of two Fe$^{3+}$ ions being not strictly equivalent.

In the present research, we measured temperature-dependent $^{57}$Fe-Mössbauer spectra of a novel mixed-valence trinuclear heterometal pentafluorobenzoate cluster complex $\text{Cr}^{3+}\text{Fe}^{3+}\text{Fe}^{2+}\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3\cdot 0.5\text{C}_5\text{H}_5\text{N}\cdot\text{CH}_2\text{Cl}_2$ by $^{57}$Fe-Mössbauer Spectroscopy.

2. Experimental

2.1. Material preparation. Chromium(III) nitrate nonahydrate (1.60 g, 4.0 mmol), iron(II) chloride tetrahydrate (0.20 g, 1.0 mmol), and pyridine (3 mL) were dissolved in ethanol (15 mL), with a molar ratio of Cr$^{3+}$ to Fe$^{2+}$ of 4.7 The mixture was stirred for 30 min, to which sodium pentafluorobenzoate (2.34 g, 10.0 mmol) was added. The resultant blackish-purple solid product was filtered and extracted with dichloromethane. The solution was stored in a refrigerator for a few weeks to yield polycrystalline product.

The sample was characterized by elemental analysis, TG-MS, IR spectroscopy and so on.

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The atomic ratio of Fe/Cr in the present complex was checked with an energy-dispersive X-ray fluorescence spectrometer, by measuring Kα X-rays of Fe and Cr emitted from the sample loaded on a piece of filter paper. Numbers and kinds of crystalline solvate molecules were determined as the above chemical formula by a TG-MS measurement.

2.2. Measurements. $^{57}$Fe-Mössbauer spectra were measured in an ordinary transmission mode against a $^{57}$Co(Rh) source with a temperature range of 78 to 298 K using a Mössbauer spectrometer, fabricated by Topologic Systems Inc. Measurement temperature was regulated by a liquid-N$_2$ cryostat of Oxford DN1726. The spectral curve fitting was carried out by using a commercially available program, MossWinn 4.0Pre. The isomer shift (IS) and Doppler velocity scale were calibrated with respect to metallic iron at 298 K.

3. Results and Discussion

Figure 2 shows the temperature-dependent Mössbauer spectra of $^{57}$Fe$^{3+}$Fe$^{2+}$O(C$_6$F$_5$COO)$_6$(C$_5$H$_5$N)$_3$·CH$_2$Cl$_2$ (1); the fitting curves are illustrated only for the spectra at 78 and 298 K. The spectral shapes at 120, 180, and 240 K are greatly complicated because of extensive line-broadening due to a relaxation effect. It is known that satisfactory fittings are impossible for such spectra by an ordinary least-square calculation method.

As seen in the figure, the spectrum at 78 K was deconvoluted into two doublets, assigned to the high-spin ferric (Fe$^{3+}$) and the high-spin ferrous (Fe$^{2+}$) species from their Mössbauer parameters summarized in Table 1. The relative ratio of Mössbauer absorption intensity (i.e., area) of Fe$^{3+}$ to Fe$^{2+}$ was evaluated to be 1.27 / 1 (=56/44), deviating somewhat from an expected ratio of unity in the chemical composition of the sample material. Such deviation might be probably due to incompleteness of valence-trapping even at 78 K, or to difference of recoilless fraction between the Fe$^{3+}$ and Fe$^{2+}$ sites. With increasing temperature, the two doublets were collapsed and then merged into only one doublet, as shown in Figure 2.

The IS and quadrupole splitting (QS) values are 0.72 mm/s and 0.43 mm/s, respectively, at 298 K (Table 1). Interestingly the IS value (0.72 mm/s) of the present heteromeric complex (1) at 298 K is obviously larger than that (0.64 mm/s) of the tri-iron complex Fe$^{3+}$Fe$^{2+}$Fe$^{2+}$O(C$_6$F$_5$COO)$_6$(C$_5$H$_5$N)$_3$·CH$_2$Cl$_2$ (2) at 300 K, as reported in our previous articles. Since the average oxidation state of the complex (2) is +2.7 [= (3+3+2)/3] assuming complete valence-detrapping among two Fe$^{3+}$ cations and one Fe$^{2+}$ cation, the larger IS value for the complex (1) at room temperature indicates that the average oxidation state should be lower than +2.7 and be presumed to be +2.5, which is probably ascribable to the fast electron hopping between only two iron cations in the CrFeFeO-complex (1). In contrast such fast hopping takes place among three iron cations in the FeFeFeO-complex (2). We tentatively presume that valence detrapping among two iron and chromium ions should not occur owing to a substantial ionizing-energy difference (M$^{3+}$ to M$^{2+}$, or M$^{2+}$ to M$^{3+}$) between iron and chromium.

Validity of our argument above is checked by comparing the observed IS values in a valence-detrapped states of the complexes (1) and (2) with those estimated as a weighted-average IS value at room temperature for Fe$^{3+}$ and Fe$^{2+}$, that is, ($IS_{Fe^{3+}}$+$IS_{Fe^{2+}}$)/2 or (2$IS_{Fe^{3+}}$+$IS_{Fe^{2+}}$)/3. However, we cannot obtain any experimental data on $IS_{Fe^{3+}}$ and $IS_{Fe^{2+}}$ at room temperature for the complexes (1) and (2), where valence-trapped states never appear at room temperature. Since the IS value of $^{57}$Fe nucleus increases with lowering the temperature due to the second Doppler shift, the degree of which is affected by complex factors, it is impossible to evaluate the room-temperature IS values of Fe$^{3+}$ and Fe$^{2+}$ using those in the trapped state of the complex (1) or (2) at lower temperature. As a first approximation, we can use the IS values of Fe$^{3+}$ and Fe$^{2+}$ of the closely-related complex Fe$^{3+}$Fe$^{2+}$Fe$^{2+}$O(C$_6$F$_5$COO)$_6$(C$_5$H$_5$N)$_3$ (3), revealed to be in a fully valence-trapped state at room temperature in our recent work. Using the observed IS values of 0.43 mm/s and 1.12 mm/s for Fe$^{3+}$ and Fe$^{2+}$, respectively, for the complex (3) at room temperature, the IS values were approximately estimated to be 0.66 mm/s for +2.7 state of the complex (2) and 0.78 mm/s for +2.5 state of the complex (1) though the estimated values are somewhat large. This discussion for the estimation is illustrated and summarized in Figure 3. The discrepancy between the observed and estimated values is
in the same direction and degree, suggesting the same origin of the discrepancy.

In summary, it is concluded from the present investigation that one d-electron transfers or hops between the Fe$^{3+}$ and Fe$^{2+}$ ions much faster than the $^{57}$Fe-Mössbauer measurement time-window of 100 ns, resulting in valence-detrapped state, i.e., Fe$^{2.5+}$, at room temperature. Thus, chromium cation Cr$^{3+}$ is left alone from the valence-detrapping; two iron cations among trinuclear metals participate in the detrapping phenomena, and the detrapping is complete, leading to Fe$^{2.5+}$.

Our finding is the first report of such “partial” and “complete” iron valence-detrapping among trinuclear metal cations to the best of our knowledge.

References and Note

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(7) When the molar ratio (Cr$^{3+}$/Fe$^{2+}$) was less than 2, the complex Cr$^{3+}$Fe$^{3+}$Fe$^{2+}$O(C$_6$F$_5$COO)$_6$(C$_5$H$_5$N)$_3$·0.5C$_5$H$_5$N·CH$_2$Cl$_2$, could not be synthesized, yielding Fe$^{2+}$Fe$^{3+}$O(C$_6$F$_5$COO)$_6$(C$_5$H$_5$N)$_3$·CH$_2$Cl$_2$, checked by Mössbauer measurements. With a reactant mixture with a molar ratio of Cr$^{3+}$-Fe$^{3+}$:Fe$^{2+}$ of 1:1:1, the CrFe$_2$O-complex was not obtained, but the Fe$_2$O-complex was formed.