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Synthesis and Mössbauer Spectroscopic Studies of Oxo-Centered Mixed-Valence Trinuclear Iron Carboxylates with Long Chain Fatty Acid Anions

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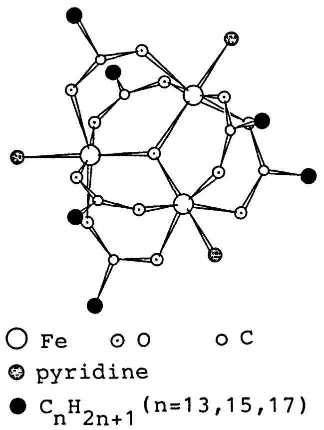
Oxo-Centered Mixed-valence trinuclear iron complexes with long chain fatty acid anions, such as myristate, palmitate, and stearate anions, were synthesized by the reaction of acetate complex, $[Fe_3O(CH_3CO_2)_6(py)_3]$ with long chain fatty acid in pyridine. XRD patterns of them show that they have a layer structure. Their Mössbauer spectra show a delocalized valence state at room temperature while a localized valence state at lower temperatures.



It is known that iron atoms in some of biferrocene compounds and oxo-centered trinuclear iron carboxylates show a temperature-dependent mixed-valence state.[1-6] Based on the results that the temperature-dependent mixed-valence state is observed in a solvated compound, for a instance, $[Fe_3O(CH_3CO_2)_6(py)_3]py$, but not in a non-solvated compound $[Fe_3O(CH_3CO_2)_6(py)_3]$, it has been concluded that the molecular motions of interstitial pyridine molecules are associated with the temperature dependence of mixed-valence state.[7] There have been few reports on the temperature dependence of mixed-valence state of iron atoms in oxo-centered trinuclear iron carboxylates other than acetates probably because of the difficulties in the preparation of the compounds,[8] and, therefore, no effects of alkyl groups of the carboxylate ligands were found on the mixed-valence state. On the other hand, it is known that some of dialkyl biferrocenium triiodides show a temperature-dependent valence state depending upon the kinds of the substituted alkyl groups and also upon the crystal structures even in the same dialkylbiferrocenium triiodides.[9-13] The present paper describes the temperature dependence of mixed-valence state of iron atoms in oxo-centered trinuclear iron myristate, palmitate, and stearate complexes which have been prepared by using a new method, in order to study the effects of alkyl groups.

The oxo-centered trinuclear iron carboxylates were synthesized by adding pyridine solution of an exess amount of myristic acid, palmitic acid and stearic acid, respectively, into a pyridine solution of $[Fe_3O(CH_3CO_2)_6(py)_3]$, which was prepared according to the literature.[14] Dark green colored precipitates were filtered and recrystallized from ethanol-pyridine. FT-IR spectra were taken to determine that acetate ligands were exchanged completely with fatty acids. The purity of the products was checked by elemental analyses. Calcd for myristate complex ($C_{99}H_{177}N_3O_{13}Fe_3$) : C, 66.61; H, 9.99; N, 2.35%. Found : C, 66.84; H, 10.10; N, 2.44%. Calcd for palmitate complex ($C_{111}H_{201}N_3O_{13}Fe_3$) : C, 68.25; H, 10.37; N, 2.15%. Found : C, 68.12; H, 10.59; N, 2.11%. Calcd for stearate complex ($C_{123}H_{225}N_3O_{13}Fe_3$) : C, 69.63; H, 10.69; N, 1.98%. Found : C, 69.59; H, 10.84; N, 1.84%.

X-Ray diffraction patterns were taken using Cu K_α radiation. Mössbauer spectra of the samples kept at various temperatures were determined in a Mössbauer spectrometer against a ^{57}Co(Rh) source moving at room temperature in an constant acceleration mode. The spectra were least-squares fit with Lorentzian lines. Velocity calibration was carried out by determining the magnetic splitting of natural iron foil, and experimental errors were estimated within ±0.01 mm s^{-1}. All the data of isomer shifts were referred with respect to metallic iron.

X-Ray diffraction patterns of the samples were shown in Fig. 1. One of the most remarkable feature of them is that the reflection lines appear with an equal interval in the small angle region, suggesting a layer structure. The inter-layer distances are estimated to be 20.9 Å in myristate, 23.2 Å in palmitate, and 25.7 Å in stearate complexes. As shown in Fig. 2, the inter-layer distance increases linearly with the increase in the number of the carbon atoms in alkyl group. The differences are found in the inter-layer distances between myristate and palmitate complexes and between palmitate and stearate complexes to be 2.3 Å and 2.5 Å, respectively, which nearly correspond to the length of two methylene groups (ca. 2.5 Å). If these compounds have a bilayer structure, the increase of inter-layer length is estimated to be more than 2.5 Å and less than 5.0 Å and the intensity of reflections in the small angle region is also expected to change alternatively. Because the intensity of the reflections decreases monotonously with increasing 2θ, it is concluded that these

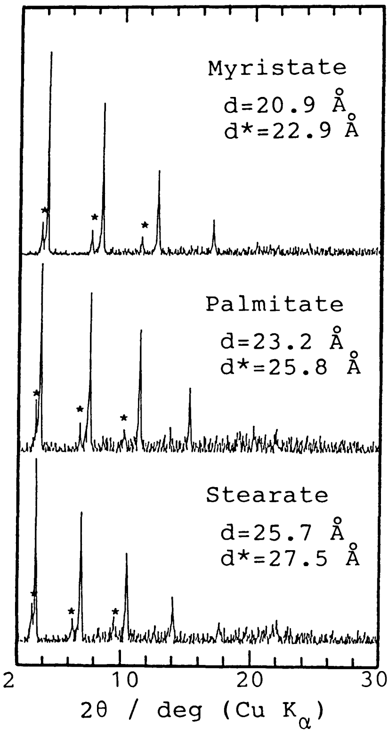


Fig. 1. XRD patterns of $[Fe_3O(RCO_2)_6(py)_3]$.

d and d* : inter-layer distance (see text)

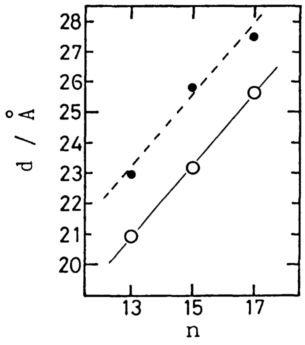


Fig. 2. Inter-layer distance in $[Fe_3O(C_nH_{2n+1}CO_2)_6(py)_3]$.

closed circle : satellite peak
open circle : main peak

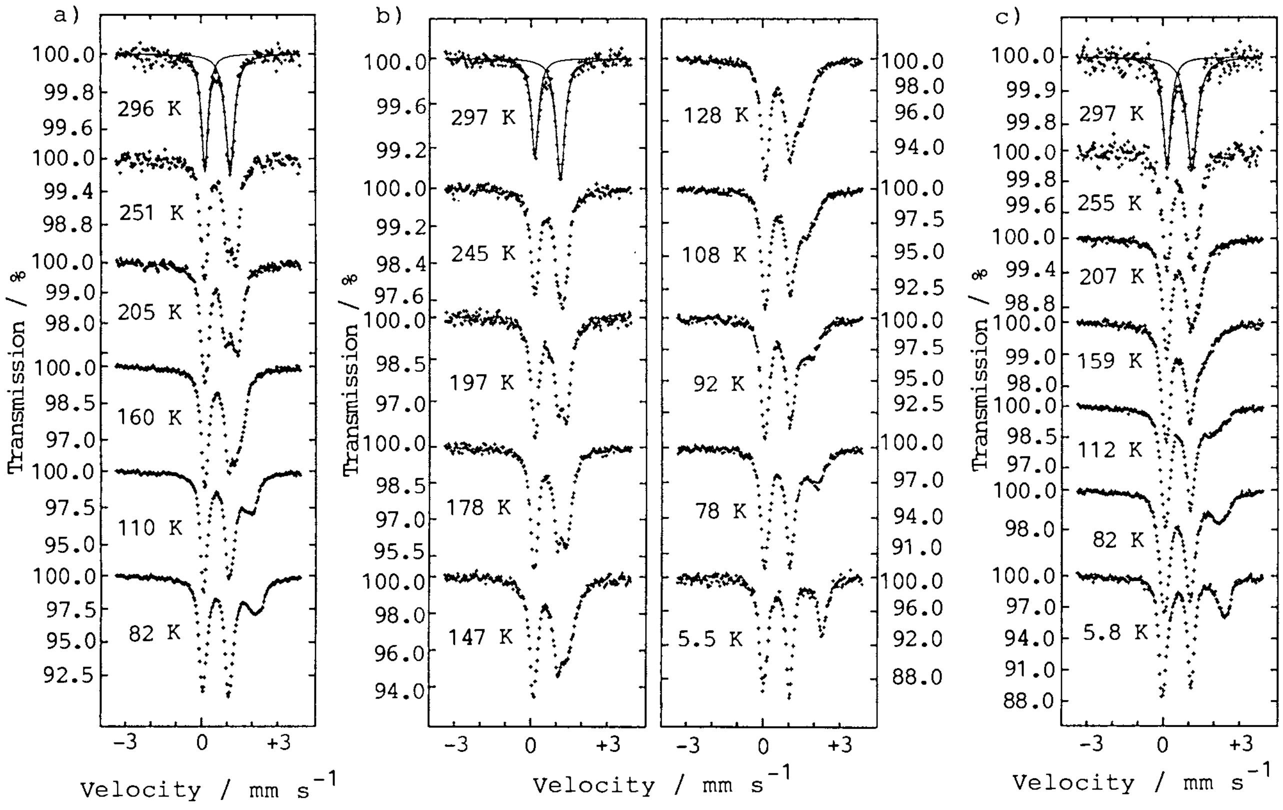


Fig. 3. Mössbauer spectra of oxo-cenered trinuclear iron a) myristate, b) palmitate, and c) stearate complexes $[Fe_3O(RCO_2)_6(py)_3]$.

compounds have a single layer structure in a solid.

Mössbauer spectra of the myristate, palmitate, and stearate complexes at various temperatures are shown in Fig. 3. All the spectra of the compounds indicate similar temperature dependences. At lower temperatures two quadrupole-split doublets are assigned to high-spin divalent iron atoms and high-spin trivalent iron atoms. With the increase of the temperature the two quadrupole-split doublets move closer together, and then become an approximately one quadrupole-split doublet at room temperature, showing an intermediate isomer-shift value of divalent and trivalent iron states, as listed in Table 1. The asymmetric intensity of each doublet is attributed to the preferential orientation of the plate-like crystalline samples mounted on a sample holder.

Table 1. Mössbauer parameters of $[Fe_3O(RCO_2)_6(py)_3]$ at room temperature

Sample	I.S. / mm s^{-1}	Q.S. / mm s^{-1}
Myristate	0.65	1.00
Palmitate	0.66	1.00
Stearate	0.66	0.99

A small portion of another phase having a little longer inter-layer distance (shown by d^* in Fig. 1) is found to coexist in each sample. These weak satellite peaks also show a similar increase in the inter-layer distance with the icreasing carbon chain in alkyl groups of the complexes in the X-ray diffraction patterns as found in Fig. 2.

According to the Debye approximation at high temperatures, the logarithmic value of recoil-free fraction of Mössbauer atoms is expected to decrease linearly with increasing temperature. However, as seen in Fig. 4, the temperature dependence of recoilfree fraction in each sample is found to deviate from the linearity, especially at higher temperatures, probably because of the increasing motions of the alkyl chains in a solid. The present results indicate that long alkyl chains in the oxo-centered trinuclear iron carboxylate complexes [$Fe_3O(RCO_2)_6(py)_3$] play an important role as well as solvate molecules in [$Fe_3O(CH_3CO_2)_6(py)_3$]py, probably by communicating intermolecular interactions associated with the valence-delocalization. It is also concluded that the length of alkyl chain of carboxylate ligands used in the present studies demonstrates no essential difference in the temperature dependences of quadrupole splitting and recoil-free fraction. Athough further investigations are needed to find the critical length of alkyl chain to show the valence-delocalization by using carboxylate ligands which have shorter alkyl chains.

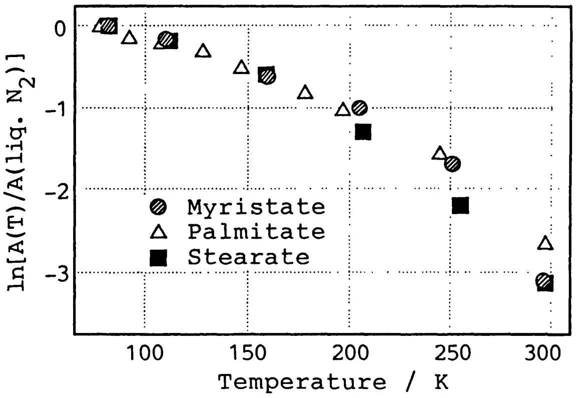


Fig. 4. Temperature dependence of recoil-free fraction.

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