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Abrupt Conversion of Mixed-Valence State in Trinuclear Iron Cyanoacetate Complex

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The crystal structure of newly synthesized trinuclear iron cyanoacetate complex, $[Fe_3O(NCCH_2CO_2)_6(H_2O)_3]$, has been determined by single-crystal X-ray structure analysis and found to have a three-dimensional hydrogen-bond network. The temperature dependence of Mössbauer spectrum shows that the complex converts from a valence-trapped state to a valence-detrapped state within a 10 K range.

Recent studies on intramolecular electron transfer in mixed-valence complexes indicate that the environmental effect in a solid is one of the most important factors in determining the rate of intramolecular electron transfer.[1-5] In the previous studies, it has been pointed out that the onset of motion of non-coordinated solvate molecules (S) can influence the rate of intramolecular electron transfer for the mixed-valence trinuclear iron acetate complexes, $[Fe_3O(CH_3CO_2)_6(L)_3]S$, where L=pyridine or its derivatives.[2] For instance, a temperature-dependent valence detrapping in the Mössbauer time-scale($\sim 10^{-7}$ s) has been observed in the pyridine-solvated acetate complex, $[Fe_3O(CH_3CO_2)_6(py)_3]py$, of which pyridine solvate molecules are found to rotate dynamically in the lattice at temperatures above ~190 K, but not in the non-solvated acetate complex, $[Fe_3O(CH_3CO_2)_6(py)_3]$. It has been confirmed for several solvated acetate complexes by heat capacity measurements that such valence detrapping occurs cooperatively in a phase transition. In addition, it has also been pointed out that the intermolecular interactions between trinuclear iron acetate complexes in a solid can cause a development of long-range order and a cooperative valence detrapping in large regions (domains) through the overlap of the terminal ligands (L). Even in the case of the first order phase transitions associated with the discontinuous Mössbauer spectral changes, a spectral conversion from a valence-trapped to a valence-detrapped state is usually observed over a broad temperature range from several tens to more than a hundred of degrees. The gradual spectral change demonstrates that the valence detrapping process involves not only first order phase transitions but also higher order phase transitions, and that a thermal

electron transfer seems to be involved in it. In the present study, a mixed-valence trinuclear iron cyanoacetate complex, $[Fe_3O(NCCH_2CO_2)_6(H_2O)_3]$, was synthesized and the crystal structure and the mixed-valence states were determined.

The cyanoacetate complex was prepared as follows. A solution of $NCCH_2CO_2H$(4.3 g, 0.05 mol) and NaOH(2.0 g, 0.05 mol) in 30 ml of water was added to a solution of $FeCl_2 \cdot 4H_2O$(5.0 g, 0.025 mol) in 20 ml of water. The mixture was allowed to stand in a shallow dish covered with a watch glass for a few weeks at room temperature. A brown needle-like crystal was used for X-ray structure analysis.[5,6] Mössbauer spectra of the sample kept at various temperatures were determined with a Mössbauer spectrometer against a $^{57}Co(Rh)$ source moving at room temperature in a constant acceleration mode. The evaluation of the spectra was made by least-squares fitting with Lorentzian lines. Velocity calibration was carried out by determining the magnetic splitting of natural iron foil. All the data of isomer shifts were referred with respect to metallic iron.

An ORTEP drawing of the molecular structure is shown in Fig. 1. The structure shows a typical triangular unit: three iron atoms with a triply bridged oxygen atom at a center, six bridged carboxylato ligands, and three coordinated H_2O ligands. The central oxygen atom placed approximately in the Fe_3 plane is located on a crystallographic three-fold symmetry axis. Because the crystal includes no extra counter anion, the formal oxidation state of the iron atoms in this complex can be described as (Fe^{III}, Fe^{III}, Fe^{II}). The oxidation state of the three iron atoms is concluded to be in an intermediate valence state between Fe^{II} and Fe^{III} at room temperature, because they are crystallographically equivalent.

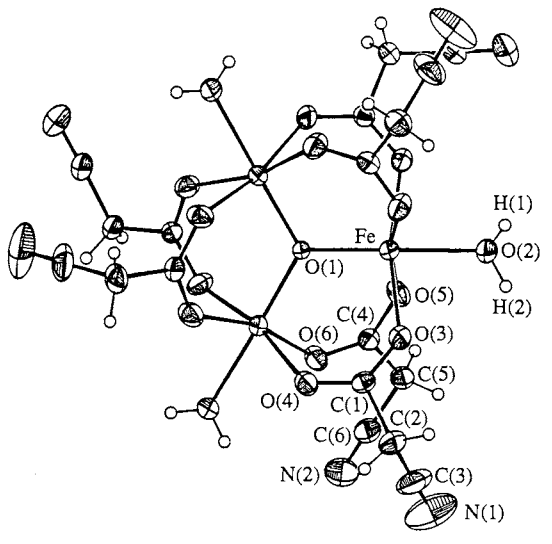

Fig. 1. Molecular structure of the complex.

Table 1. Selected bond lengths and angles

Bond lengths / Å			
Fe - O(1)	1.8951(3)	C(1) - C(2)	1.522(3)
Fe - O(2)	2.124(2)	C(2) - C(3)	1.446(3)
Fe - O(3)	2.066(1)	C(3) - N(1)	1.119(5)
Fe - O(4)	2.062(1)	C(4) - C(5)	1.518(2)
Fe - O(5)	2.055(1)	C(5) - C(6)	1.455(4)
Fe - O(6)	2.071(1)	C(6) - N(2)	1.127(2)
O(3) - C(1)	1.245(3)		
O(4) - C(1)	1.249(3)	(Intermolecular)	
O(5) - C(4)	1.248(3)	N(1)···O(2)	2.916(4)
O(6) - C(4)	1.249(3)	N(2)···O(2)	2.851(2)
Bond angles / deg			
O(1) - Fe - O(2)	178.59(5)	(Intermolecular)	
O(1) - Fe - O(3)	96.24(6)	C(3) - N(1)···O(2)	121.2(3)
O(1) - Fe - O(4)	96.23(7)	C(6) - N(2)···O(2)	167.1(2)
O(1) - Fe - O(5)	95.42(7)	N(1)···H(1) - O(2)	168(2)
O(1) - Fe - O(6)	97.62(6)	N(2)···H(2) - O(2)	177(3)

The conformation of the cyanoacetato ligands with respect to the Fe_3O plane is quite different, forming two different types of intermolecular hydrogen bond between the terminal

N atoms and the water ligands of the adjacent molecules (see Table 1 and Fig. 2). The type I hydrogen bond is formed between N(1) and H(1) atoms of an invertible molecular pair related with a center of symmetry, whereas the type II is formed between N(2) and H(2) atoms of a superimposable molecular pair. Total nine neighboring molecules are directly linked to one molecule through the intermolecular hydrogen bonds; three are by type I and six are by type II. Figure 2 illustrates only asymmetric one-third part of an entire set having three-fold symmetry. Because of the equivalency for all the molecules in the whole crystal, it has been acknowledged that two types of hydrogen bonds form an infinite three dimensional network.

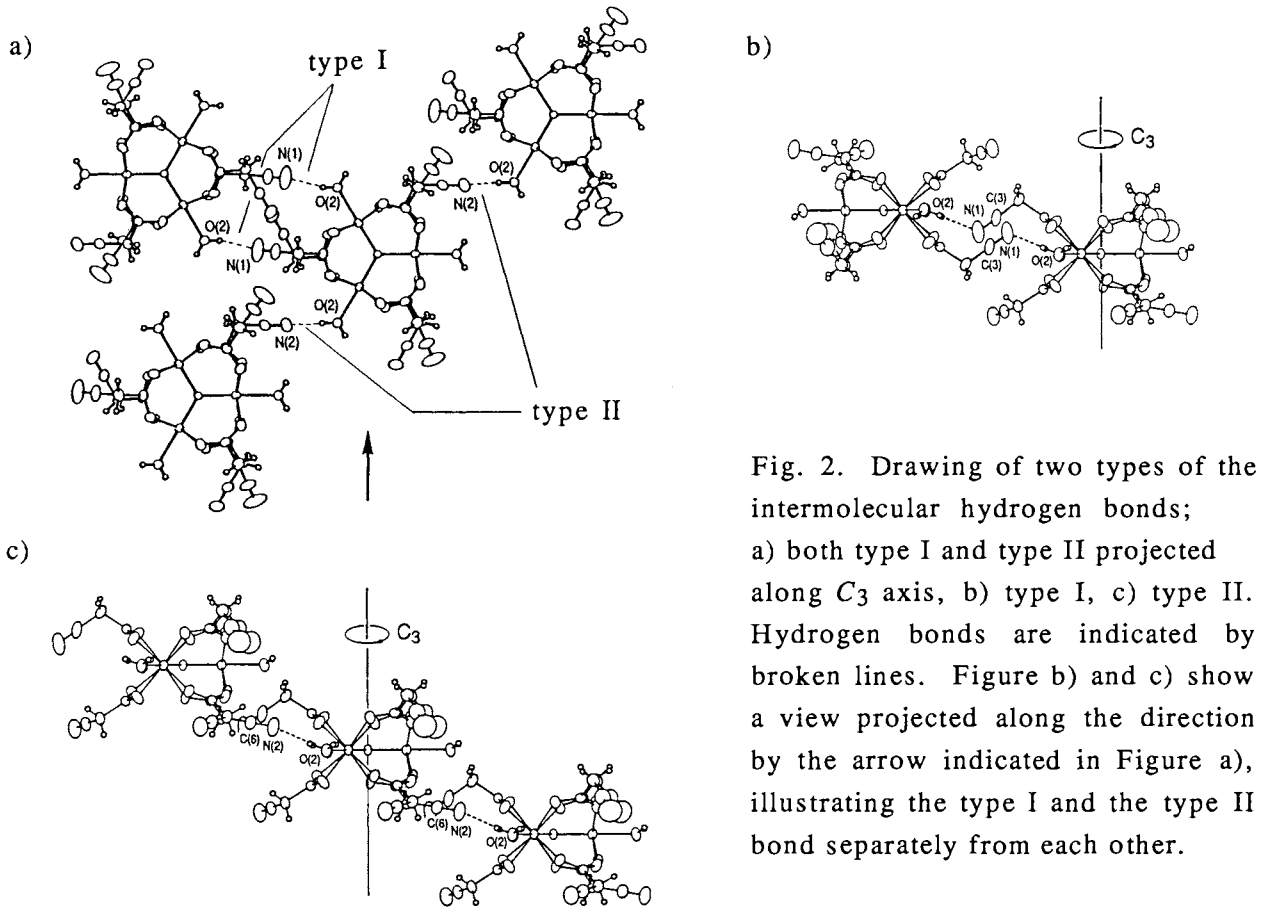

Fig. 2. Drawing of two types of the intermolecular hydrogen bonds; a) both type I and type II projected along C_3 axis, b) type I, c) type II. Hydrogen bonds are indicated by broken lines. Figure b) and c) show a view projected along the direction by the arrow indicated in Figure a), illustrating the type I and the type II bond separately from each other.

Mössbauer spectra of the complex are shown in Fig. 3.[8] At temperatures below 125 K, two quadrupole-split doublets ascribed to a high-spin Fe^{II} and a high-spin Fe^{III} are observed with an area ratio of ~1:2. At temperatures between 129 K and 132 K, the spectrum abruptly changes to only one quadrupole-split doublet, although it is difficult to fit the Mössbauer spectra to available Lorentzian lines in this temperature range. At temperatures above 133 K, there is only one quadrupole-split doublet ascribed to an intermediate valence state between Fe^{II} and Fe^{III}. The temperature dependence of the recoil-free fraction of the Mössbauer spectrum and the DSC measurements have certificated that a first order phase transition occurs at temperatures around ~130 K.

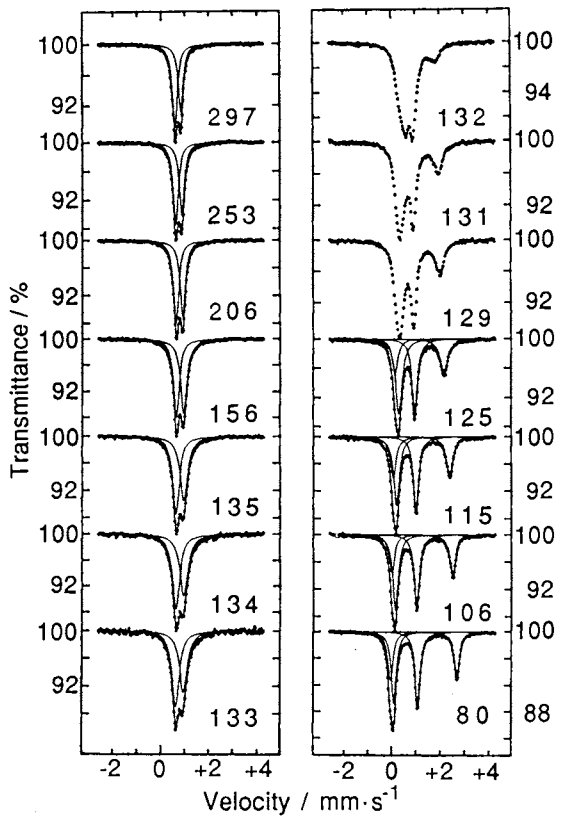

Fig. 3. Mössbauer spectra of the complex.

Our recent studies have also demonstrated that the non-solvated Fe_3O complexes, such as butyrate,[5] myristate, palmitate, and stearate complexes[3,4] also show a valence detrapping accompanied by phase transitions, suggesting that direct intermolecular interactions through the alkyl chains can also influence the rate of intramolecular electron transfer principally. The abrupt change found in the temperature dependence of valence state in a narrower temperature range indicates that the intermolecular interactions through hydrogen bond is strong enough to cause the valence transformation catastrophically compared with the intermolecular interactions developed through solvate molecules or alkyl groups.

For further clarification, the crystal structure analysis at temperatures below ~130 K and the heat capacity measurement will be carried out in the near future.

References

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3) T. Nakamoto, M. Katada, and H. Sano, *Chem. Lett.*, **1990**, 225.
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6) Anal. Found: C, 29.39; H, 2.25; N, 11.23%. Calcd for $Fe_3C_{18}H_{18}O_{16}N_6$: C, 29.14; H, 2.45; N, 11.33%.
7) Crystal data: $[Fe_3O(NCCH_2CO_2)_6(H_2O)_3]$, rhombohedral, space group $R\bar{3}$ (# 148); a= 20.026(1) Å, c=12.292(2) Å, V=4269.1(9) Å^3; Z=6; d_{calc}=1.73 g/cm^3; μ=15.9 cm^{-1}. Total 1384 independent reflections with $|F_o| > 3\sigma|F_o|$ ($5.0° < 2\theta < 52.6°$) collected at room temperature with Mo K_α(0.71073 Å) radiation on an Enraf-Nonius CAD-4 diffractometer were used for calculation. The structure was solved by direct methods(SIR 88) and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms to a final R, R_w=0.020, 0.029.
8) Mössbauer parameters: ΔE_Q=0.250(3), δ=0.695(1) mm/s at 297 K. ΔE_Q=0.986(2), δ=0.573(1) mm/s, and ΔE_Q=2.743(3), δ=1.299(1) mm/s at 80 K.

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