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Mixed-valence States of ^{57}Fe Atoms Produced in ^{57}Co-labelled $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ and $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$

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Mixed-valence states of ^{57}Fe atoms produced by EC-decay in ^{57}Co-labelled $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ and $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$ were studied by means of emission Mössbauer spectroscopy. It was found that $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ and $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$ show a temperature-dependent trapped-to-averaged valence state and a temperature-independent trapped-valence state, respectively.

Recently we have reported that ^{57}Fe atoms produced by EC-decay in ^{57}Co-labelled $[Co^{II}Fe_2^{III}O(CH_3CO_2)_6(H_2O)_3]$ and $[Co^{II}Fe_2^{III}O(CH_3CO_2)_6(py)_3]py$ show a temperature-dependent trapped-to-averaged valence state associated with the intramolecular electron transfer as found in the absorption Mössbauer spectra of $[Fe^{II}Fe_2^{III}O(CH_3CO_2)_6(H_2O)_3]$ and $[Fe^{II}Fe_2^{III}O(CH_3CO_2)_6(py)_3]py$, respectively.[1)] It has been also reported in the absorption ^{57}Fe-Mössbauer spectroscopy that the temperature dependence of the mixed-valence state in trinuclear iron complexes depends on a kind of ligands such as H_2O and pyridine, and of carboxylate anions.[2,3)] The temperature dependence observed in trinuclear iron complexes can be calssified into two groups, a temperature-dependent trapped-to-averaged valence type and a temperature-independent trapped valence type. In the present paper we describe the mixed-valence state of ^{57}Fe atoms produced by the EC-decay in ^{57}Co-labelled $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ and $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$ studied by means of emission Mössbauer spectroscopy, in order to confirm that ^{57}Fe atoms produced by the ^{57}Co EC-decay in trinuclear cobalt-iron complexes remain in the original chemical environment of the parent ^{57}Co atoms for typical compounds which show either a temperature-dependent or a temperature-independent mixed-valence state. The valence state of iron atoms in the trinuclear iron complexes, $[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$, $[Fe_3O(CH_2BrCO_2)_6(H_2O)_3]$ and $[Fe_3O(CH_{3-n}Cl_nCO_2)_6(H_2O)_3]$ ($0 \leq n \leq 3$) was also investigated for the sake of comparison of the results with the emission Mössbauer spectroscopic data.

^{57}Co-labelled $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ and $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$ were synthesized by the way similar to that reported for non-radioactive $[CoFe_2O(CH_3CO_2)_6(H_2O)_3]$ except for using CH_2ICO_2Na and CH_2BrCO_2Na instead of CH_3CO_2Na and using ca. 1 mCi $^{57}Co(NO_3)_2$ solution.[2] An aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ was added dropwise to a mixture of an aqueous solution of CH_2ICO_2Na (or CH_2BrCO_2Na) and $Co(NO_3)_2 \cdot 6H_2O$ containing ^{57}Co. Resulting precipitates were filtered and washed with ethanol and ethyl ether.

$[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$, $[Fe_3O(CH_2BrCO_2)_6(H_2O)_3]$, $[Fe_3O(CH_2ClCO_2)_6(H_2O)_3]$, $[Fe_3O(CHCl_2CO_2)_6(H_2O)_3]$ and $[Fe_3O(CCl_3CO_2)_6(H_2O)_3]$ were prepared by the partial oxidation of an aqueous solution of $FeCl_2 \cdot 4H_2O$ mixed with CH_2ICO_2Na, CH_2BrCO_2Na, CH_2ClCO_2Na, $CHCl_2CO_2Na$ and CCl_3CO_2Na, respectively, in the presence of air. Resulting precipitates were filtered and washed with ethanol and ethyl ether. The purity of the labelled compounds was checked by comparing the data of elemental analysis obtained in a cold run in the same scale for each compound. The purity of trinuclear iron complexes was also checked by elemental analysis. Emission and absorption Mössbauer spectra were taken by using a constant acceleration type spectrometer. All the velocity scales were normalized with respect to metallic iron.

It has been reported that the temperature dependence of the valence state

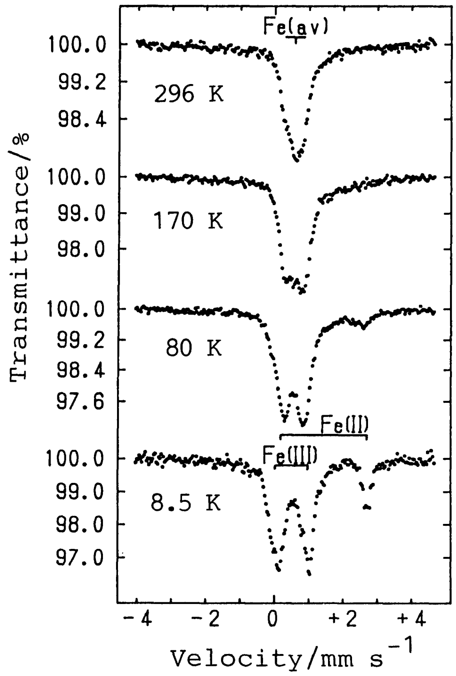

Fig. 1. Absorption Mössbauer spectra of $[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$.

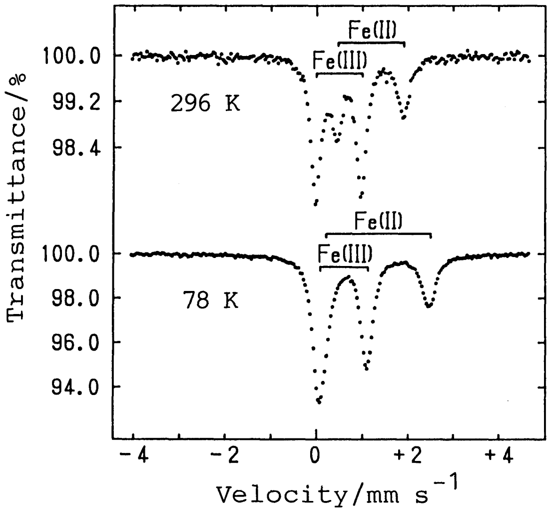

Fig. 2. Absorption Mössbauer spectra of $[Fe_3O(CH_2BrCO_2)_6(H_2O)_3]$.

in trinuclear iron acetate complexes is affected by the substitutions of acetate anions with a long-chain carboxylate anions or of water molecules with pyridine and pyridine derivative molecules.[2,3] It is found in the present studies that the halogenation of acetate anions also affects the temperature dependence of mixed-valence state in iron atoms in $[Fe_3O(CH_3CO_2)_6(H_2O)_3]$, $[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$, $[Fe_3O(CH_2BrCO_2)_6(H_2O)_3]$ and $[Fe_3O(CH_{3-n}Cl_nCO_2)_6(H_2O)_3]$. $[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$ and $[Fe_3O(CCl_3CO_2)_6(H_2O)_3]$ show a temperature-dependent trapped-to-averaged valence state as in the case of $[Fe_3O(CH_3CO_2)_6(H_2O)_3]$, while $[Fe_3O(CH_2BrCO_2)_6(H_2O)_3]$, $[Fe_3O(CH_2ClCO_2)_6(H_2O)_3]$, and $[Fe_3O(CHCl_2CO_2)_6(H_2O)_3]$ show a temperature-independent trapped valence state. Typical absorption Mössbauer spectra are represented in Figs. 1 and 2 for $[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$ and $[Fe_3O(CH_2BrCO_2)_6(H_2O)_3]$, respectively. The electron withdrawing property of the carboxylate groups is known to increase in the order of $CH_3CO_2^- < CH_2ICO_2^- < CH_2BrCO_2^- < CH_2ClCO_2^- < CHCl_2CO_2^- < CCl_3CO_2^-$, but the temperature dependence does not correspond to the order. The results indicate that the intermolecular interaction predominates rather than the electron withdrawing property of the ligand in the rate of the intramolecular electron transfer, as suggested in the studies of trinuclear long-chain carboxylate complexes.[3] A more detailed discussion on the valence state

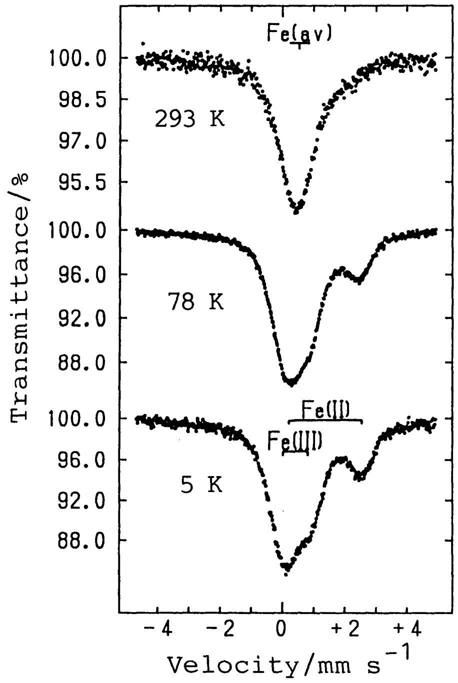

Fig. 3. Emission Mössbauer spectra of ^{57}Co-labelled $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$.

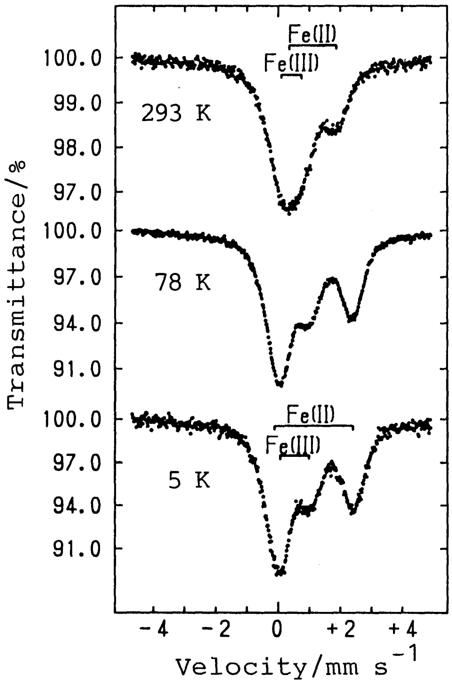

Fig. 4. Emission Mössbauer spectra of ^{57}Co-labelled $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$.

of these complexes will be given elsewhere.

In the cases of trinuclear cobalt-iron complexes, $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ and $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$ which are isomorphous to the analogous trinuclear iron complexes $[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$ and $[Fe_3O(CH_2BrCO_2)_6(H_2O)_3]$, respectively, it is confirmed by the absorption Mössbauer spectroscopic studies that the valence state of iron atoms remains in a temperature-independent trivalent state.

Emission Mössbauer spectra of ^{57}Co-labelled $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ are shown in Fig. 3. The valence state of ^{57}Fe atoms produced by the EC-decay of ^{57}Co in $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ is found to be temperature-dependent as found in the absorption Mössbauer spectra of $[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$ (Fig. 1), although the line width of spectral components in the emission Mössbauer spectra is much broader than that found in the absorption Mössbauer spectra probably because of nucleogenic local disturbance associated with the EC-decay.$^{4-7)}$ Emission Mössbauer spectra of ^{57}Co-labelled $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$ show that the temperature dependence is essentially different from that observed in $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$, as seen in Fig. 4, and that the ^{57}Fe atoms are trapped in iron(II) and iron(III) states even at room temperature. Since the temperature dependence of the valence states observed in ^{57}Co-labelled $[CoFe_2O(CH_2ICO_2)_6(H_2O)_3]$ and $[CoFe_2O(CH_2BrCO_2)_6(H_2O)_3]$ corresponds to that observed in $[Fe_3O(CH_2ICO_2)_6(H_2O)_3]$ and $[Fe_3O(CH_2BrCO_2)_6(H_2O)_3]$, it is reasonable to conclude that the EC-decay should have little after effect particularly on the mixed-valence state, although some local disturbances are produced by the nuclear transformation. The authors thank Tadahiro Nakamoto for his interest and helpfull discussions.

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