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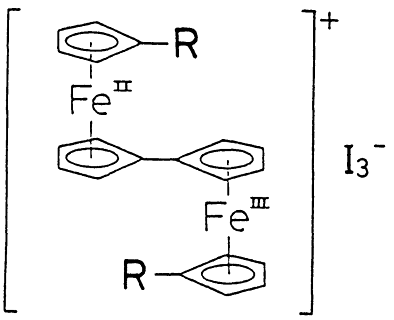
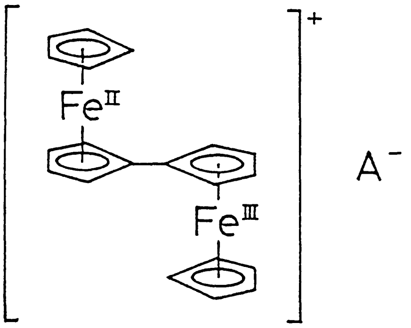
^{57}Fe-Mössbauer Spectroscopic Studies of Mixed-valence Binuclear Ferrocenes with Various Metal Complex Anions

Masahiro KAI,* Motomi KATADA, and Hirotoshi SANO*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukasawa, Setagaya-ku, Tokyo 158

Mixed-valence binuclear ferrocenium salts with $FeCl_4^-$, $SnCl_6^{2-}$, and $ZnCl_4^{2-}$ anions were studied by using ^{57}Fe-Mössbauer spectroscopy. The $FeCl_4^-$ and $SnCl_6^{2-}$ salts show two types of the temperature dependence of the spectra, whereas the $ZnCl_4^{2-}$ salt shows no temperature dependence, concluding that the valence state of iron atoms does not depend on the chemical nature of binuclear ferrocenyl cations but on the interactions through the cations and the anions in solid.

It has been found in ^{57}Fe-Mössbauer spectroscopic studies that the valence state of iron atoms depends upon temperature in some mixed-valence binuclear ferrocenyl triiodides, such as 1',1'''-diethylbiferrocenium (**1**), 1',1'''-di-n-propylbiferrocenium (**2**),[1] 1',1'''-di-n-butylbiferrocenium (**3**),[2] and biferrocenium triiodides (**4**).[3] It is also known that most mixed-valence binuclear ferrocenyl salts fall into two main categories according to the temperature dependence of their Mössbauer spectra. In one category, two doublets are shown in a Mössbauer spectrum at low temperatures, ascribed to Fe(II) and Fe(III) states, which approach to each other with increasing the temperature to merge into one doublet ascribed to an averaged-valence state (e.g., **1**, **2**, and **3**). In another category, the third doublet ascribed to an averaged-valence state





1: $R=CH_2CH_3$
2: $R=CH_2CH_2CH_3$
3: $R=CH_2CH_2CH_2CH_3$

4: $A^-=I_3^-$
5: $A^-=FeCl_4^-$
6: $A^-=\frac{1}{2}SnCl_6^{2-}$
7: $A^-=\frac{1}{2}ZnCl_4^{2-}$

grows with increasing the temperature in addition to the two doublets at low temperatures until the two doublets finally fade out at high temperatures (e.g., 4). In the present studies, three kinds of mixed-valence biferrocenium salts with $FeCl_4^-$ (5), $SnCl_6^{2-}$ (6), and $ZnCl_4^{2-}$ (7) were synthesized in order to clarify the intramolecular electron-transfer and the intermolecular interactions by using the same binuclear ferrocenyl cation that shows the two types of temperature dependence of the valence state. The temperature dependence of the valence state of iron atoms was determined by using ^{57}Fe-Mössbauer spectroscopy.

Biferrocene was prepared by the method previously reported.[4] Mixed-valence biferrocenium salts with $FeCl_4^-$, $SnCl_6^{2-}$, and $ZnCl_4^{2-}$ anions were prepared as follows.[5] A mixture of biferrocene and p-benzoquinone (2:1 in molar ratio) was dissolved in a sufficient amount of benzene/hexane (2:1) at 0 °C. To this solution a methanol solution dissolving a stoichiometric amount of metal chloride ($FeCl_3$ for 5, $SnCl_4 \cdot 5H_2O$ for 6, $ZnCl_2$ for 7) and an excess amount of concentrated hydrochloric acid was added with vigorous stirring at 0 °C. The black precipitates were filtered, washed with cold benzene, and dried in vacuo. Found: C, 42.65; H, 3.02%. Calcd for the $FeCl_4^-$ salt (5), $C_{20}H_{18}Fe_3Cl_4$: C, 42.40; H, 3.18%. Found: C, 44.76; 3.61%. Calcd for the $SnCl_6^{2-}$ salt (6), $C_{40}H_{36}Fe_4SnCl_6$: C, 44.90; H, 3.37%. Found: C, 51.77; H, 4.03%. Calcd for the $ZnCl_4^{2-}$ salt (7), $C_{40}H_{36}Fe_4ZnCl_4$: C, 50.07; H, 3.80%.

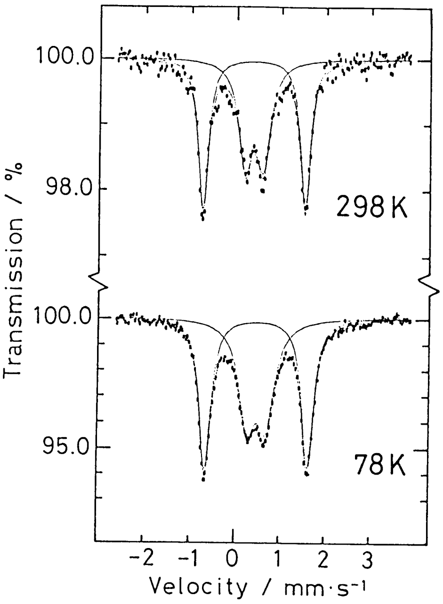


Fig. 1. ^{57}Fe-Mössbauer spectra of biferrocenium $ZnCl_4$ salt, 7.

The ^{57}Fe-Mössbauer spectra of 5, 6, and 7 were determined at temperature between 78 and 298 K. The valence state of the iron atoms of the $ZnCl_4^{2-}$ salt, 7, does not seem to depend upon temperature. As shown in Fig. 1, only two doublets can be seen both at 298 and 78 K; one outer doublet having a larger quadrupole splitting (Q.S.) and the other inner doublet having a smaller Q.S. are ascribed to ferrocene-like Fe(II) and ferricinium-like Fe(III), respectively.

In contrast to the spectra of 7, the valence states of the iron atoms of 5 and 6 found from their Mössbauer spectra depend upon temperature, although the types of temperature dependences differ from each other as follows. As illustrated in Fig. 2, the ^{57}Fe-Mössbauer spectra of the $SnCl_6^{2-}$ salt, 6, show only two doublets ascribed to Fe(II) and Fe(III) at 78 K. With increasing the temperature of 6, the third doublet ascribed to an averaged-valence state grows in addition to the two doublets. At 210 K, only one doublet can be found, indicating that all iron atoms sit in the averaged-valence state. The same type of temperature dependence is found in biferrocenium I_3, Br_2I,[3] and I_2Br.[6]

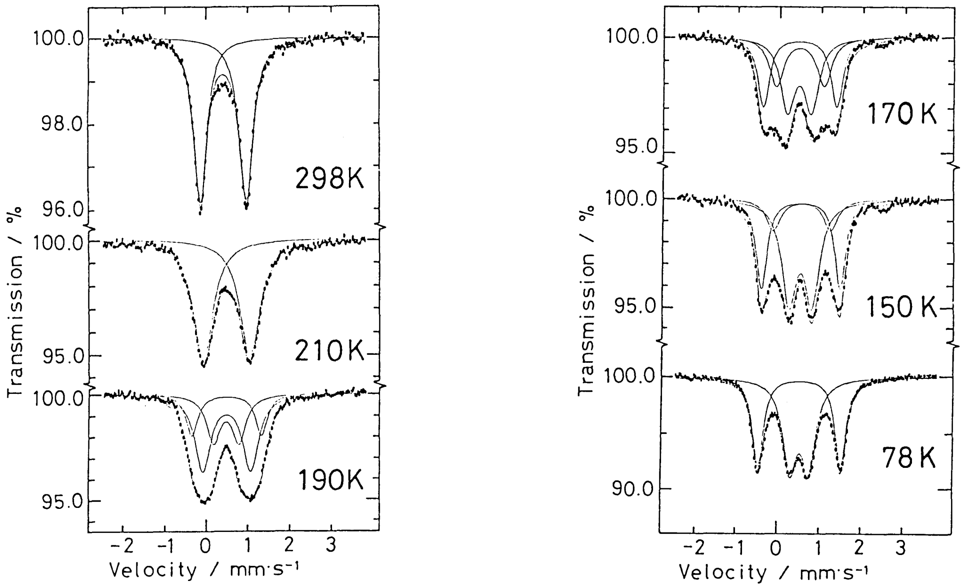


Fig. 2. ^{57}Fe-Mössbauer spectra of biferrocenium $SnCl_6$ salt, 6.

As seen in Fig. 3, the Mössbauer spectra of the $FeCl_4^-$ salt, 5, show two doublets with an outer large Q.S. and an inner small Q.S. and one singlet with an unresolvable small Q.S. at 78 K, which are ascribed to ferrocene-like Fe(II),

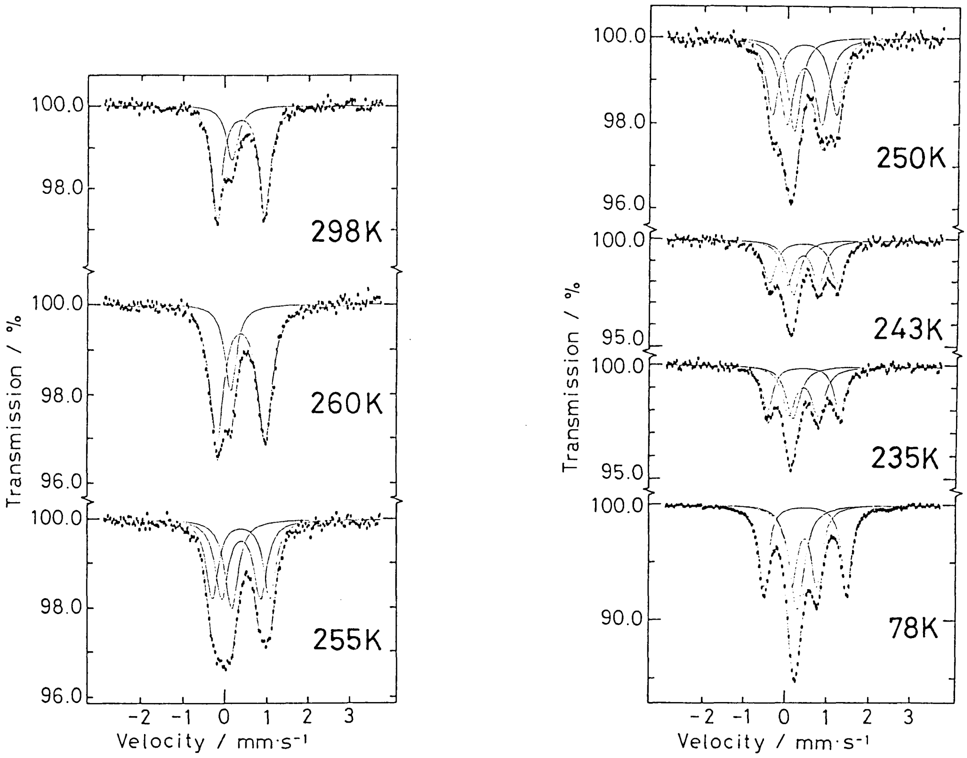


Fig. 3. ^{57}Fe-Mössbauer spectra of biferrocenium $FeCl_4$ salt, 5.

ferricinium-like Fe(III) in biferrocenium cations, and high-spin Fe(III) species in tetrachloroferrate(III) anions, respectively. The two doublets found at 78 K approach to each other with increasing temperature, to merge into one doublet ascribed to an averaged-valence state at 260 K. In the spectra at any temperatures the "third doublet" ascribed to an averaged-valence state in **6** does not appear besides the two doublets ascribed to trapped-valence states in biferrocenium cations. The singlet of the tetrachloroferrate(III) anions is found at all temperatures from 78 K to 298 K, showing no temperature dependence in the Q.S. values. This type of temperature dependence of the biferrocenium cations in **5** is the first example for the cations having no alkyl substituents. It is also the first case that the same binuclear ferrocenyl cation shows the two types of temperature dependence of the valence states according to the kinds of counter anions.

The results provide us with the conclusion that the valence state of iron atoms does not depend on the chemical nature of binuclear ferrocenyl cations but probably on the interactions through the cations and the anions in solid.

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