CHEMISTRY LETTERS, pp. 1523-1526, 1988.

^{57}Fe-Mössbauer Spectroscopic Studies of a New Series of Mixed-valence Biferrocenium Salts

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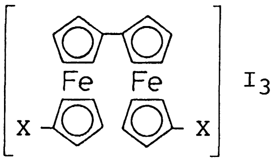
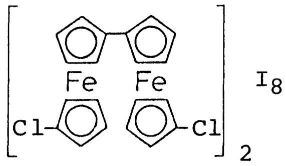
Biferrocenium and 1',1'''-dihalobiferrocenium tetrachloroferrate(III) and dibromocuprate(I) were prepared by a new method. It was found by ^{57}Fe-Mössbauer spectroscopy that the valence states of their iron atoms and the temperature dependence were quite different from those of the corresponding biferrocenium and 1',1'''-dihalobiferrocenium triiodide salts.

It is known in the salts prepared by oxidizing biferrocene and 1',1'''-dihalobiferrocene with iodine that the iron atoms are found in either an averaged-valence state or a trapped-valence state, showing one doublet or two doublets, respectively, on their ^{57}Fe-Mössbauer spectra. The iron atoms of 1',1'''-dibromobiferrocenium triiodide (**1**)$^{1)}$ and 1',1'''-diiodobiferrocenium triiodide (**2**)$^{2)}$ show one doublet even at 4.2 K, whereas those of biferrocenium triiodide (**3**)$^{3)}$ and 1',1'''-dichlorobiferrocenium octaiodide(2-) (**4**)$^{1)}$ show two doublets assigned to iron(II) and iron(III) at any temperatures below 298 K. In the case of 1'-chloro-1'''-iodobiferrocenium triiodide (**5**), the spectrum shows one doublet at temperatures from 4.2 to 298 K as in the cases of 1',1'''-dibromo- and 1',1'''-diiodobiferrocenium triiodides.$^{4)}$ The iron atoms in 1',1'''-di-n-butylbiferrocenium triiodide are known to show two types of the temperature dependence of valence state depending on the crystal form of the salt; in one crystal form the iron atoms remain in a trapped-valence state, whereas in the other they change the valence state from a trapped-valence state to an averaged-valence state from at lower temperatures to at higher temperatures.$^{5)}$ It has been pointed out that the valence states of iron atoms in biferrocenyl derivatives salts are essentially affected by crystal structure and that the substituents of cyclopentadienyl rings are less effective.$^{4,6)}$ The present studies were planned to clarify the effects of anions other than I_3^- or I_8^{2-}. Mono-oxidized mixed-valence salts of biferrocenium and



1: X=Br, **2**: X=I
3: X=H



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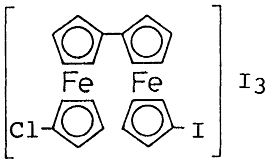

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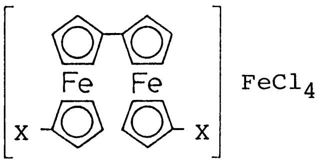
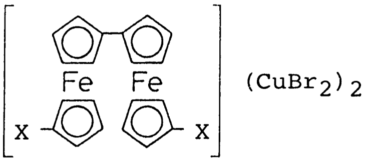
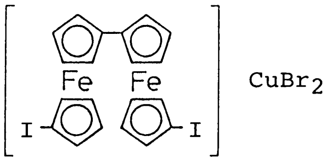


6: X=H, 7: X=Br
8: X=I



9: X=H, 10: X=Br



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1',1'''-dihalobiferrocenium having $FeCl_4^-$ or $CuBr_2^-$ as a counter anion were tried to prepare by a new method described below, because the salts of binuclear ferricinium cations with $FeCl_4^-$ and $CuBr_2^-$ anions are not known and 2,3-dichloro-5,6-dicyanoquinone and tetrafluoroborate oxidize both the two iron atoms of binuclear ferrocenes.

Biferrocene and 1',1'''-dihalobiferrocene were prepared by the method previously reported.[7,8] The $FeCl_4^-$ salts of these compounds were prepared as follows: A mixture of biferrocenyl derivatives and p-benzoquinone (1.0/0.5 in molar ratio) was dissolved in a sufficient amount of benzene/hexane (2:1) at 0 °C. To this solution a methanol solution prepared by dissolving a stoichiometric amount of iron(III) chloride and an excess amount of concentrated hydrochloric acid was added with vigorous stirring at 0 °C. The black or dark-green precipitates thus obtained were filtered, washed with benzene, and dried in vacuo. The $CuBr_2^-$ salts were prepared in the same way by using copper(I) bromide and hydrobromic acid instead of iron(III) chloride and hydrochloric acid, respectively. Found: C, 42.23; H, 3.23%. Calcd for 6, $C_{20}H_{18}Fe_3Cl_4$: C, 42.40; H, 3.18%. Found: C, 31.03; H, 2.07%. Calcd for 7, $C_{20}H_{16}Fe_3Cl_4Br_2$: C, 33.15; H, 2.21%. Found: C, 28.41; H, 1.88%. Calcd for 8, $C_{20}H_{16}Fe_3Cl_4I_2$: C, 29.27; H, 2.21%. Found: C, 28.40; H, 2.37%. Calcd for 9, $C_{20}H_{18}Fe_2Cu_2Br_4$: C, 29.41; H, 2.22%. Found: C, 24.64; H, 1.74%. Calcd for 10, $C_{20}H_{16}Fe_2Cu_2Br_6$: C, 24.65; H, 1.65%. Found: C, 27.98; H, 2.01%. Calcd for 11, $C_{20}H_{16}Fe_2CuBr_2I_2$: C, 28.42; H, 1.91%.

Although the $FeCl_4^-$ and $CuBr_2^-$ salts of 1',1'''-dichlorobiferrocene were not obtained, biferrocene, 1',1'''-dibromobiferrocene, and 1',1'''-diiodobiferrocene formed 1:1 salts with $FeCl_4^-$ anions and 1',1'''-diiodobiferrocene gave a 1:1 salt with a $CuBr_2^-$ anion in much better yields (e.g., 73% for biferrocenium $FeCl_4$ and 70% for 1',1'''-diiodobiferrocenium $CuBr_2$) even compared with the yield of ferricinium $FeBr_4$ salt by the method previously reported (47%).[9] ^{57}Fe-Mössbauer spectra of these salts proved that they were mono-oxidized mixed-valence compounds. As illustrated in Figs. 1, 2, and 3, the spectra of 6, 7, and 8 at 78 K consist of two doublets assigned to iron(II) and iron(III) atoms in the cations and one doublet with a very small quadrupole splitting assigned to high-spin iron (III) atoms of $FeCl_4^-$ anions. The isomer shift and the quadrupole splitting values of iron(II) atoms of biferrocenium cations in the $FeCl_4^-$ salt, 6, are found to be 0.54 mm s^{-1} and 2.03 mm s^{-1} and those of iron(III) are 0.52 mm s^{-1} and 0.60 mm s^{-1}, respectively, which are determined based on least-squares fitted Lorentzian line shapes. These parameters are close to the isomer shift and the quadrupole splitting values of iron(II), 0.53 and 2.09 mm s^{-1}, and of iron(III), 0.54 and 0.39 mm s^{-1}, in biferrocenium triiodide salt. On the other hand, the

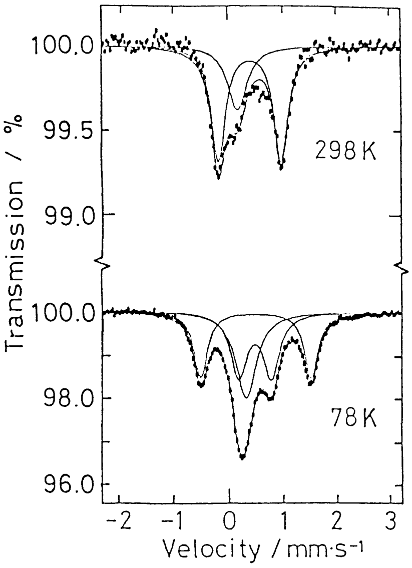

Fig. 1. ^{57}Fe-Mössbauer spectra of biferrocenium $FeCl_4$, 6.

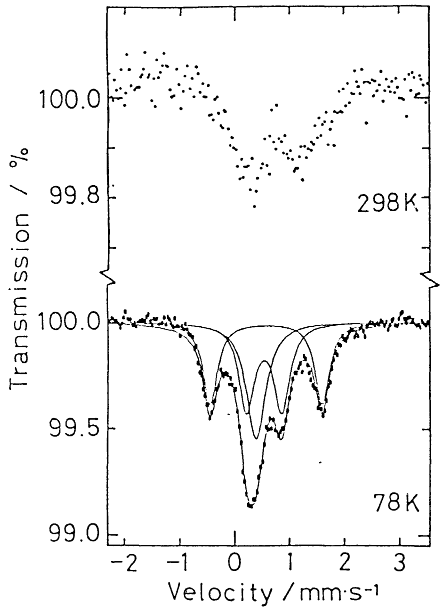

Fig. 2. ^{57}Fe-Mössbauer spectra of 1',1'''-dibromobiferrocenium $FeCl_4$, 7.

spectral features of salts, 6, 7, and 8 at 298 K are quite different from those of corresponding triiodides, 3, 1, and 2, respectively. The two iron atoms in a 1',1'''-diiodobiferrocenium cation of 8 show two doublets on the spectrum at 298 K (Fig. 3), whereas the two iron atoms in the I_3^- salt, 2, give one doublet at temperatures from 4.2 to 298 K. The two iron atoms in a biferrocenium cation of 6 show one doublet on the spectrum at 298 K (Fig. 1), whereas two doublets are observed in biferrocenium triiodide, 3, at temperatures from 4.2 to 298 K. The results indicate that the transition temperatures, at which two doublets turn into one doublet, be found to be lower in 6 than that of the I_3^- salt, 3 (in the case of 3, the transition temperature is found above 300 K).[10] As illustrated in Fig. 2, the spectrum of 7 at 298 K is not very clear because of poor counting statistics associated with Mössbauer-γ-ray absorption by bromine atoms but the two iron atoms in a 1',1'''-dibromobiferrocenium cation of 7 seem to have at least a component assigned to an averaged-valence state in addition to a component of $FeCl_4^-$.

As illustrated in Fig. 4, 1',1'''-diiodobiferrocenium $CuBr_2$, 11, at 78 K shows an averaged-valence state giving one doublet similar to the I_3^- salt, 2 (at 78 K, although the quadrupole splitting value of the spectrum of 11 is a little smaller (1.23 mm s^{-1}) than the value of 2 (1.40 mm s^{-1})[1]). The spectrum of the $CuBr_2^-$ salt, 11, at 4.2 K shows two doublets, whereas the two iron atoms of the I_3^- salt, 2, show only one doublet even at 4.2 K. In the cases of oxidation of biferrocene and 1',1'''-dibromobiferrocene, 1:2 salts with $CuBr_2^-$ anions were obtained. The Mössbauer spectra of these salts, 9 and 10, show only one singlet assigned to a ferricinium-like iron(III), indicating that both the iron atoms in a biferrocenium or a 1',1'''-dibromobiferrocenium cation were completely oxidized. No mixed-valence state is found in 9 and 10 at any temperatures.

The results indicate that the valence state of iron atoms in a new series of

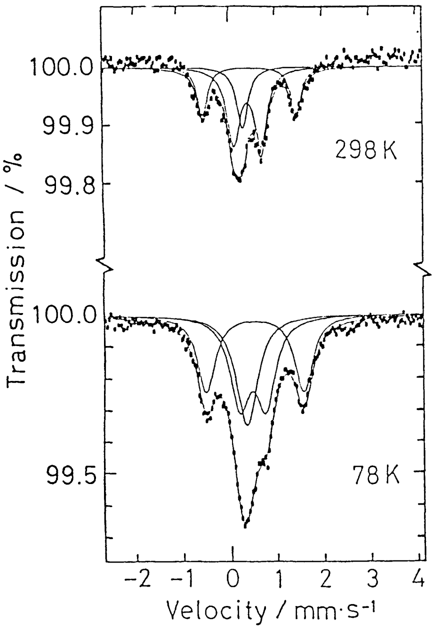

Fig. 3. ^{57}Fe-Mössbauer spectra of 1',1'''-diiodobiferrocenium $FeCl_4$, 8.

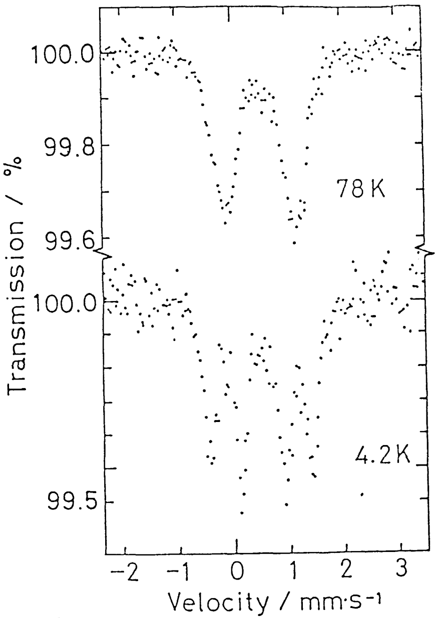

Fig. 4. ^{57}Fe-Mössbauer spectra of 1',1'''-diiodobiferrocenium $CuBr_2$, 11.

binuclear ferricinium salts with $FeCl_4^-$ and $CuBr_2^-$ anions depends upon the kinds of counter anions probably because the crystal structure of the mixed-valence binuclear ferricinium salts is affected by the properties of anions. For instance, the tetrahedral $FeCl_4^-$ anions introduced as counter anions instead of linear I_3^- anions may change the interactions among cations and/or anions from the cases of I_3^- salts, causing different valence states of iron atoms.

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(Received June 16, 1988)