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MÖSSBAUER SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES ON 1',1'''-DIHALOBIFERROCENES

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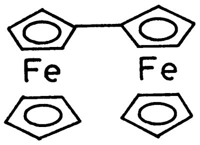
In the Mössbauer spectroscopic studies on the triiodide salts of a series of 1',1'''-dihalobiferrocenes, it has been found that the monocations of diiodo- and dibromobiferrocene show averaged valence states of iron atoms, while the monocation salt of dichlorobiferrocene shows a trapped valence state of iron atoms. On the other hand, no difference has been found in the half-wave potentials of the halobiferrocenes.

Since Cowan and his co-workers discovered that monooxidized biferrocene exhibits an intramolecular interaction between ferrocene and ferricenium moieties,1, 2) many kinds of binuclear ferrocene derivatives have been examined by means of various physicochemical measurements and some of them have been recognized as suitable compounds for the investigation of the mixed valence phenomena.3, 4)



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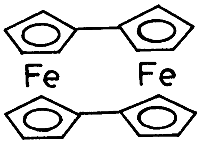

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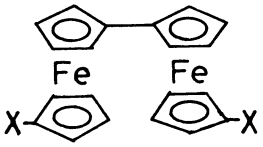

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These monocation salts can be classified into the following two categories, trapped valence type and averaged valence type compounds by means of Mössbauer spectroscopy.5) For example, the monocation salt of biferrocene (1) and biferrocenylene (2), which are two of the simplest members of binuclear ferrocenes among the mixed valence compounds, show the Mössbauer spectra characteristic of a trapped valence type and an averaged type compound, respectively.6, 7) The former has two kinds of the valence state of iron atoms corresponding to Fe(II) and Fe(III), while the latter has only an equivalent state of iron atom averaging over the two kinds of valence states on the Mössbauer time scale. Recently, Hendrickson et al. reported that the triiodide salt of 1',1'''-diiodobiferrocene (3, X = I) monocation also shows the averaged valence state of the iron atom in the Mössbauer spectra at 4.2 K and 300 K, while various monocation salts of biferrocene (1) itself are of the trapped valence type in the temperature range from 4.2 to 300 K.8)

It was reported in the previous paper that the monocation salts of 1',1'''-dialkylbiferrocenes show a remarkable temperature dependence of the valence state of iron atoms on the ^{57}Fe Mössbauer time scale.9) Namely, Mössbauer spectra of 1',1'''-diethyl- and 1',1'''-dipropylbiferrocene monocations are of the averaged valence type above 275 K and 260 K, respectively, and of the trapped valence type below about 200 K.

In the course of the Mössbauer spectroscopic studies on the mixed valence phenomena of binuclear ferrocene derivatives, the effect of the halogen substituted biferrocene has been studied by means of Mössbauer spectroscopy and cyclic voltammetry.

1',1'''-Dihalobiferrocene were prepared by the reaction of 1,1'-dilithioferrocene with the corresponding tosyl halide for dibromo- and dichlorobiferrocene and with iodine for diiodobiferrocene according to the procedure reported previously.10) Oxidation of the dihalobiferrocene was carried out by treating it with iodine equivalent to 2/3 of the corresponding dihalobiferrocene in dry benzene.

^{57}Fe-Mössbauer measurements were carried out by using a ^{57}Co(Pt) source moving in a constant acceleration mode. Isomer shift values were determined relative to metallic iron foil. The experimental errors in the isomer shift and the quadrupole splitting values were estimated to be ±0.02 mm/s.

Cyclic Voltammograms of the dihalobiferrocenes were obtained using a Hokuto Denki HB-107A function generator and a Hokuto Denki HA-201 potentiostat combined with a standard three-electrode configuration. A working electrode, a platinum button (Beckman) and an Ag/AgCl reference electrode, were connected via a salt-bridge containing n-Bu_4NClO_4 (0.1 M) in CH_3CN. The half-wave potentials given in Table 1 were estimated from the peak potentials.

Table 1. CV data of 1',1'''-dihalobiferrocenes and related compounds

Compound	$E_{1/2}(\underline{1})$ (V)	$E_{1/2}(\underline{2})$ (V)	$\Delta E_{1/2}$ (V)
Dichlorobiferrocene	0.51	0.81	0.30
Dibromobiferrocene	0.51	0.81	0.30
Diiodobiferrocene	0.49	0.81	0.31
Biferrocenylene[a]	0.265	0.855	0.590
Biferrocene	0.36	0.68	0.32

a) Ref. 11.

All the dihalobiferrocenes studied here undergo two successive reversible one-electron oxidations to yield the corresponding mono- and dications, respectively. The half-wave potentials are summarized in Table 1 together with those of biferrocene and biferrocenylene. The halogen substitution of biferrocene results in an increase of about 0.15 V in both of the half-wave potentials, $E_{1/2}(\underline{1})$ and $E_{1/2}(\underline{2})$, although the difference, $\Delta E_{1/2}$, between $E_{1/2}(\underline{1})$ and $E_{1/2}(\underline{2})$ remains constant, 0.30 - 0.31 V, in the series of biferrocene derivatives. On the other hand, biferrocenylene, whose monocation exhibits an averaged valence state of iron atoms on Mössbauer spectroscopy, shows a larger value of $\Delta E_{1/2}$, 0.590 V, which indicates an extraordinarily large stability of the monocation against further oxidation compared with that of biferrocene monocation.

Table 2. Mössbauer parameters of 1',1'''-dihalobiferrocenium triiodides

Compound	Temp (K)	IS[a)] (mm s^{-1})	QS (mm s^{-1})
Dichlorobiferrocenium$^+I_3^-$	78	0.52	2.08
		0.54	0.54
	200	0.48	2.07
		0.50	0.49
	298	0.46	1.95
		0.49	0.49
Dibromobiferrocenium$^+I_3^-$	4.2	0.53	1.40
	78	0.52	1.38
	298	0.49	1.23
Diiodobiferrocenium$^+I_3^-$ [b)]	4.2	0.532	1.388
	300	0.428	1.284

a) Relative to iron foil.

b) Ref. 8.

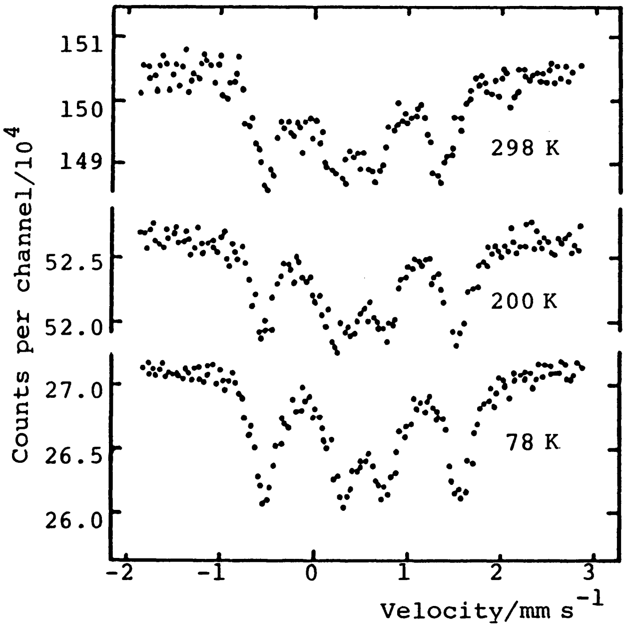

Fig. 1. Mössbauer spectra of 1',1'''-dichlorobiferrocenium$^+I_3^-$.

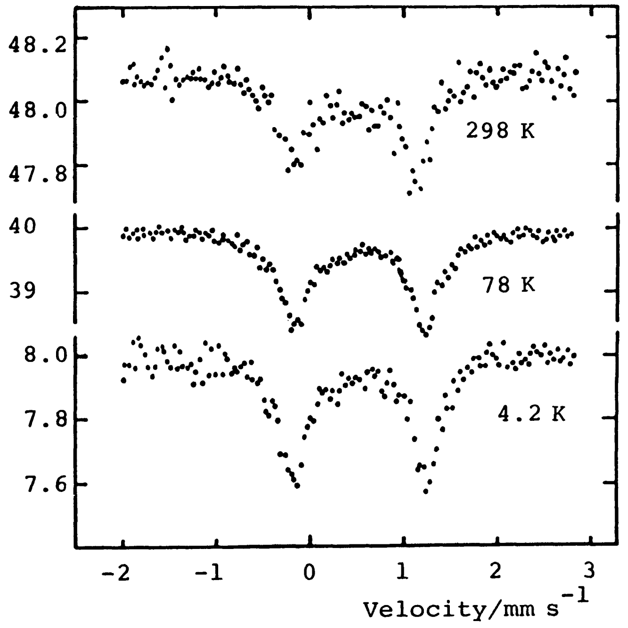

Fig. 2. Mössbauer spctra of 1',1'''-dibromobiferrocenium$^+I_3^-$.

Mössbauer parameters of the dihalobiferrocenes are listed in Table 2 and Mössbauer spectra of dichloro- and dibromobiferrocene monocation triiodide are shown in Figs. 1 and 2, respectively. As mentioned above, the Mössbauer spectra for the triiodide salt of 1',1'''-diiodobiferrocene monocation measured at 4.2 K and 300 K are typical for the averaged valence type compound consisting of only one quadrupole-split doublet. Thus, the intervalence electron transfer rate between the two iron atoms in this compound is considered to be greater than 10^7 s^{-1} even at 4.2 K. In contrast to this, the Mössbauer spectra for the monocation salt of 1',1'''-dichlorobiferrocene, as is shown in Fig. 1, are of the trapped valence type at the temperatures from 78 K to 298 K.

The triiodide salt of the dibromobiferrocene shows the averaged valence type Mössbauer spectra in the same temperature region, as in the case of diiodobiferrocene. The Mössbauer parameters for the dibromobiferrocene monocation salt are quite similar to those for the diiodobiferrocene monocation salt; that is, the isomer shifts are 0.53 mm/s and 0.49 mm/s for the former and 0.532 mm/s and 0.428 mm/s for the latter at 4.2 K and 300 K, respectively, and the quadrupole splittings are 1.40 mm/s and 1.23 mm/s for the former and 1.388 mm/s and 1.284 mm/s for the latter at 4.2 K and 300 K, respectively. In the case of the dichloro derivative, careful inspection of the Mössbauer spectra clearly indicates that there is no temperature dependence of the valence state of iron atoms as those observed for the 1',1'''-dialkylbiferrocene monocations.

The results indicate that iodine and bromine substitution in both the cyclopentadienyl rings in biferrocenium triiodides can stabilize the averaged valence state of iron atoms compared with chlorine and hydrogen atoms. It is also found that the value of half-wave potential has nothing to do with the criterion for classification of the type of valence state in a series of binuclear mixed valence ferrocene derivatives, although its possibility has once been proposed.11)

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