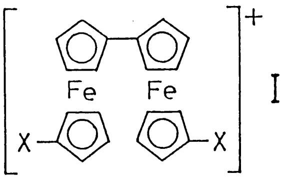
CHEMISTRY LETTERS, pp. 1037-1040, 1988.

Effects of the Halogen Substituents on the Valence State of Iron Atoms in Some Mixed-valence Dihalobiferrocenes

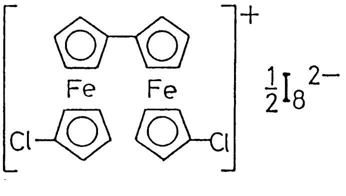
Masahiro KAI,* Izumi MOTOYAMA,† Motomi KATADA, Yuichi MASUDA,
and Hirotoshi SANO*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan
University, Fukasawa, Setagaya-ku, Tokyo 158
†Department of Chemistry, Faculty of Engineering, Kanagawa
University, Rokkakubashi, Kanagawa-ku, Yokohama 221

The mixed-valence triiodide salts of 1',1'"-dihalobiferrocenes having two different kinds of halogen substituents were synthesized. Their ^{57}Fe-Mössbauer spectra showed an averaged-valence state; i.e., one doublet even at 4.2 K, as found in the triiodide salts of 1',1'"-dibromo- and 1',1'"-diiodobiferrocenes.

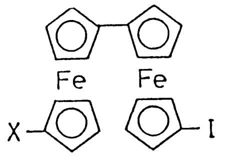
In our previous ^{57}Fe-Mössbauer spectroscopic studies of the mixed-valence salts, 1',1'"-dibromobiferrocenium I_3 (1) and 1',1'"-dichlorobiferrocenium $0.5I_8$ (2),1) it was found that the spectrum of 2 at 298 K showed two doublets, one ascribed to Fe(II) and the other to Fe(III), whereas 1 showed an averaged-valence state having one doublet even at 4.2 K. This indicates that the rate of electron transfer between the two iron atoms in 1 is faster than 10^7 s^{-1}, while that is slower than 10^7 s^{-1} in 2. The Mössbauer spectrum of 1',1'"-diiodobiferrocenium I_3 (3) was also reported to show only one doublet even at 4.2 K.2) The crystal structure of 3 is essentially the same as that of 1 but not as that of 2.3) It has been reported that 1',1'"-di-n-butylbiferrocenium I_3 shows two types of the valence states on the Mössbauer spectra as its crystal structure changes from one form to another.4) In order to clarify the effects of the halogen substituents on the valence state of iron atoms, 1'-bromo-1'"-iodobiferrocene (4) and 1'-chloro-1'"-iodobiferrocene (5) were synthesized and the valence states of iron atoms in their mono-oxidized triiodide salts, 6 and 7 respectively, were investigated by using ^{57}Fe-Mössbauer spectroscopy.



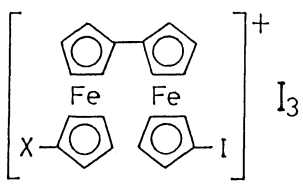
1. X=Br
3. X=I



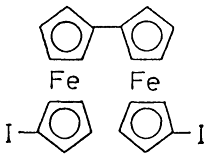
2.



4. X=Br
5. X=Cl



6. X=Br
7. X=Cl



8.

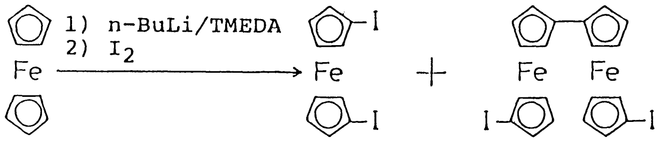
The neutral compound 4 or 5 was synthesized as follows: 1',1'"-Diiodobiferrocene (8), synthesized by the method previously reported,[5)] and copper(I) bromide or chloride, respectively, were stirred in pyridine at 110 °C for three hours. Then the reaction products were extracted repeatedly by benzene. The benzene-extracts thus obtained were washed with 10% hydrochloric acid and water. The compound 4 or 5 was isolated from the concentrated extracts by column chromatography on alumina and purified by recrystallization from benzene. ^{1}H-NMR (CDCl$_3$) for 4 (see Fig. 1) δ=3.93(2H,t), 3.98(2H,t), 4.16(4H,t), 4.23(2H,t), 4.27 (2H,t), 4.35(2H,t), 4.40(2H,t), and for 5 (Fig. 2) δ=3.89(2H,t), 3.98(2H,t), 4.14 (2H,t), 4.16(2H,t), 4.23(2H,t), 4.28(2H,t), 4.34(2H,t), 4.42(2H,t).

The I_3 salts, 6 and 7, were prepared by the one-electron oxidation of 4 and 5 by iodine in benzene, respectively. Anal. Calcd for 6, $C_{20}H_{16}Fe_2BrI_4$: C,25.1; H,1.7%. Found: C,25.4; H,2.5%. Calcd for 7, $C_{20}H_{16}Fe_2ClI_4$: C,26.34; H,1.76%. Found: C,26.48; H,1.82%.

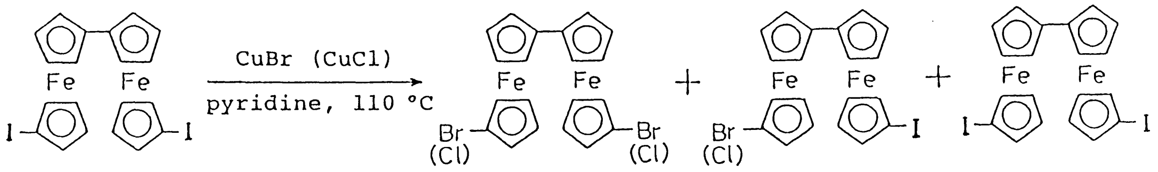
Comparison of the powder X-ray diffraction patterns for 6 and 7 with those for 1 and 2 revealed that both 6 and 7 had essentially the same crystal structures as 1 and 2.

The ^{57}Fe-Mössbauer spectra for 6 and 7 are shown in Figs. 3 and 4, respectively. Even at 4.2 K, only one doublet is seen in each spectrum of these two compounds. This shows that the rates of the electron transfer between the two iron atoms in both 6 and 7 are faster than 10^7 s^{-1}, similar to those found in 1 and 3. The Mössbauer parameters estimated by a least-squares fitting with Lorentian line shapes are given in Table 1. The quadrupole splittings and the isomer shifts of 6 and 7 are almost the same as those of 1 and 3.

The fact that the ^{57}Fe-Mössbauer parameters of 1 are similar to those of 3 clearly indicates that there is little difference between the effects of bromo and iodo substituents on the valence states of two iron atoms in a biferrocenium cation. The effect of asymmetric substitution observed in 1'-bromo-1'"-iodobiferrocenium I_3, 6, is considered to be too small to affect either the crystal structure or the valence state of iron atoms, because the crystal structures of



n-BuLi: n-Butyl lithium / TMEDA: N,N,N',N'-Tetramethylethylenediamine



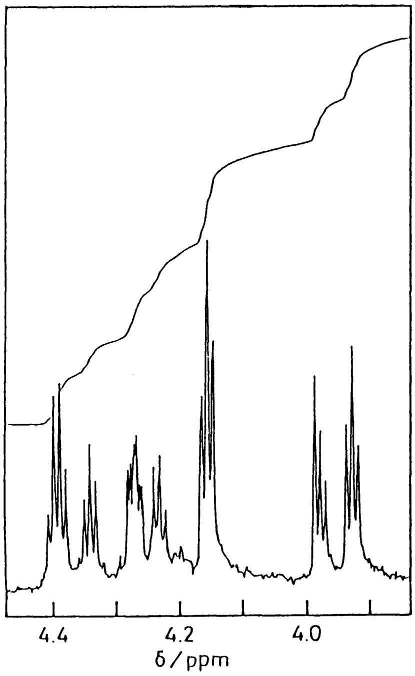


Fig. 1. ^1H-NMR spectrum of 1'-bromo-1'"-iodobiferrocene ($CDCl_3$).

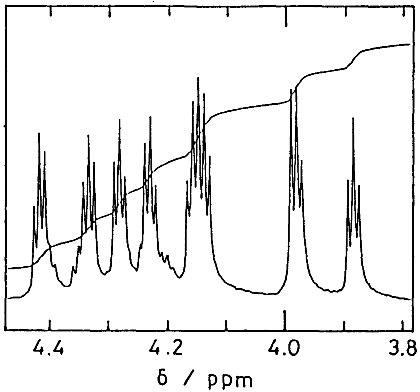


Fig. 2. ^1H-NMR spectrum of 1'-chloro-1'"-iodobiferrocene ($CDCl_3$).

1',1'"-dibromo- and 1',1'"-diiodobiferrocenium I_3 are isomorphous. But, even in the case of 1'-chloro-1'"-iodobiferrocenium I_3, **7**, the effect of chloro substitution is not very large enough to change the crystal structure from that of 1',1'"-diiodobiferrocenium I_3 and then the valence state. The compounds **1**, **3**, **6**, and **7** are all isostructural and are considered to have a suitable environment where the biferrocenium cations are brought into the position favorable to have the averaged-valence states of iron atoms in each cation. Therefore, it may be

Table 1. ^{57}Fe-Mössbauer parameters

Compound			Temp	I.S.	Q.S.	Γ.
X	Y	Anion	K	$mm \cdot s^{-1}$	$mm \cdot s^{-1}$	$mm \cdot s^{-1}$
Br	I	I_3^-	298.0	0.44	1.33	0.33 , 0.40
			78.0	0.54	1.45	0.59 , 0.55
			4.2	0.55	1.45	0.52 , 0.51
Cl	I	I_3^-	298.0	0.43	1.26	0.34 , 0.35
			78.0	0.52	1.36	0.52 , 0.50
			4.2	0.53	1.39	0.55 , 0.51
Br	Br	I_3^- 1)	298.0	0.49	1.23	
			78.0	0.52	1.38	
			4.2	0.53	1.40	
I	I	I_3^- 2)	300.0	0.428	1.284	0.257, 0.244
			4.2	0.532	1.388	0.339, 0.343
Cl	Cl	I_8^{2-} 1)	298.0	0.46	1.95	
				0.49	0.49	
			78.0	0.52	2.08	
				0.54	0.54	

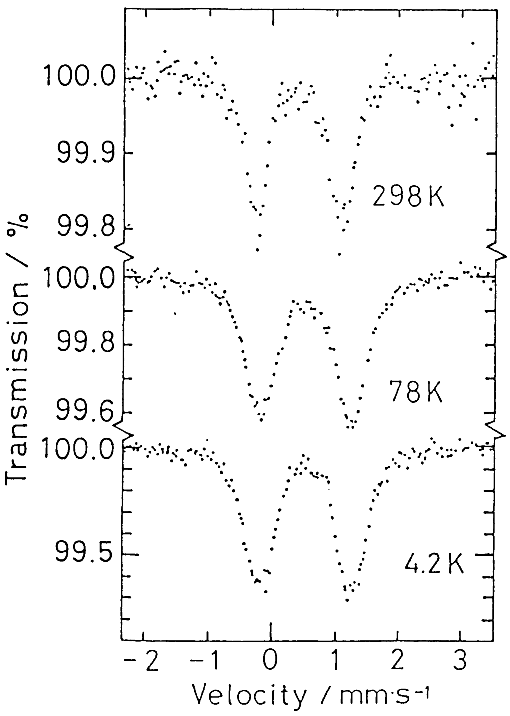


Fig. 3. ^{57}Fe-Mössbauer spectra of 1'-bromo-1'''-iodobiferrocenium I_3.

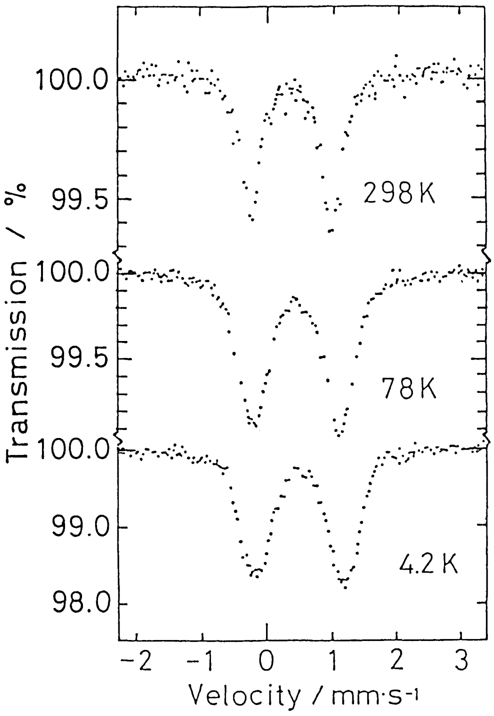


Fig. 4. ^{57}Fe-Mössbauer spectra of 1'-chloro-1'''-iodobiferrocenium I_3.

possible to expect that some salts of 1',1'''-dichlorobiferrocenium would show an averaged-valence state of iron atoms on their Mössbauer spectrum.

The authors are grateful to the Ministry of Education, Science, and Culture for a Grant-in-Aid for Scientific Research (No. 61470011).

References

1) I. Motoyama, K. Suto, M. Katada, and H. Sano, Chem. Lett., 1983, 1215.
2) W. H. Morrison, Jr. and D. N. Hendrickson, Inorg. Chem., 14, 2331 (1975).
3) T. -Y. Dong, D. N. Hendrickson, C. G. Pierpoint, and M. F. Moore, J. Am. Chem. Soc., 108, 963 (1986).
4) S. Nakashima, Y. Masuda, I. Motoyama, and H. Sano, Bull. Chem. Soc. Jpn., 60, 1673 (1987).
5) R. F. Kovar, M. D. Rausch, and H. Rosenberg, Organomet. Chem. Syn., 1. 173 (1970/1971).

(Received March 31, 1988)