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^{57}Fe-Moessbauer Spectroscopic Studies of the Ferrocenylruthenocenium$^+$BF$_4^-$ Salts

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Ferrocenylruthenocene reacts with sulfuric acid-NH_4BF_4 to give a diamagnetic ferrocenylruthenocenium$^+$BF$_4^-$ salt, while it reacts with benzoquinone-$BF_3(Et_2O)$ to give a paramagnetic ferrocenylruthenocenium^{3+}(BF$_4^-$)$_3$ salt. Based on the results of ^{57}Fe-Moessbauer spectroscopic studies, the Moessbauer parameters of the former salt are very similar to those of neutral ferrocenylruthenocene, suggesting that the structure of the salt is assumed to be $[Cp(C_5H_4)Fe(C_5H_4)Cp$-Ru-$RuCp(C_5H_4)Fe(C_5H_4)Cp]^{2+}(BF_4^-)_2$ in the solid state.

It is well-known that most ferrocene derivatives are oxidized by appropriate oxidizing agents such as benzoquinone and iodine, giving paramagnetic ferrocenium salts. A broad singlet line is found in the ^{57}Fe-Moessbauer spectra of the most ferrocenium salts.$^{1)}$ On the other hand, ruthenocene reacts with halogen such as iodine and bromine, giving diamagnetic dark-red precipitates analyzed as $[Ru(Cp)_2X]X_3$ (X; I, Br) with Ru-X bond based on the results of X-ray analysis.$^{2)}$ Ferrocenylruthenocene has a structure of ferrocene bound with a ruthenocene moiety.$^{3)}$ Although it has recently been reported that ferrocenylruthenocene reacts with some Lewis acid species such as $HgCl_2$, $SnCl_4$, and I_2, giving adducts with chemical bonds (Fe-Hg, Ru-Hg, Ru-Sn, and Ru-I) based on the results of ^{57}Fe- and ^{119}Sn-Moessbauer and ^{13}C-CP-MAS NMR spectroscopic studies,$^{4-8)}$ there has no report on the ferrocenylruthenocenium salts. The present study was planned to provide information about the chemical state of Fe atoms in the ferrocenylruthenocenium cation by means of ^{57}Fe-Moessbauer spectroscopy and other physicochemical measurements.

Ferrocenylruthenocene reacts with a stoichiometric amount of benzoquinone and BF_3-Et_2O in dry hexane mixed with benzene and gives dark brown products. The products were recrystallized from nitromethane mixed with ether and analyzed as ferrocenylruthenocenium^{3+}(BF$_4^-$)$_3$. Found; C, 35.09; H, 3.33%. Calcd for $C_{20}H_{18}FeRuB_3F_{12}$; C, 35.55; H, 2.68%. The precipitates of ferrocenylruthenocenium$^+$BF$_4^-$ were prepared by dissolving the ferrocenylruthenocene (100 mg) in 2 cm^3 of concentrated H_2SO_4. The green solution was allowed to stand at room temperature for 15 min.; then it was cooled in ice. The cold solution was filtered and the filtrate was added to a concentrated aqueous solution of NH_4BF_4. The solid formed was filtered and washed with H_2O and dried in vacuo over P_2O_5. The products were analyzed as ferrocenylruthenocenium$^+$BF$_4^-$. Found; C, 48.80; H, 4.06%. Calcd for $C_{20}H_{18}FeRuBF_4$;

C, 47.84; H, 3.61%. All the products related in the present study were confirmed by ^1H-, ^{13}C-NMR and ir-spectroscopies. ^{57}Fe-Moessbauer spectroscopic measurements were carried out by using a $^{57}Co(Rh)$ source moving in a constant acceleration mode. The isomer shift (I. S.) value for the ^{57}Fe was taken with respect to metallic iron and the experimental error of the I. S. and quadrupole splitting (Q. S.) values was estimated within ±0.02 mm s^{-1}. Cyclic voltammograms were obtained by using a Hokuto Denko HB-107 A function generator and a Hokuto Denko HA-201 potentiostat combined with a standard three-electrode configuration. A working electrode of platinum button (Beckman) and Ag/AgCl reference electrode were connected via a salt bridge of CH_3CN containing (0.1 mol dm^{-3})$[(C_4H_9)_4N]ClO_4$.

Typical ^{57}Fe-Moessbauer spectra of ferrocenylruthenocene, ferrocenylruthenocenium$^{3+}(BF_4^-)_3$ and ferrocenylruthenocenium$^+BF_4^-$ are shown in Figs. 1 and 2, respectively, and ^{57}Fe-Moessbauer parameters are listed in Table 1. The Q. S. and I. S. values of ferrocenylruthenocene well correspond to the values of biferrocene (as shown in Table 1). The fact shows that the ruthenocene moiety has little effect on the electronic state of ferrocene moiety in neutral ferrocenylruthenocene.

The results of ^{57}Fe-Moessbauer study of the ferrocenylruthenocenium$^{3+}(BF_4^-)_3$ salt show that well-dissolved large Q. S. values are observed at temperatures from 4.2 to 300 K, although most of the ferrocenium salts only show a broad singlet line in their spectra because of fast relaxation, as seen in ferrocenium$^+BF_4^-$ salt (Fig 2-d). The results of ESR studies show that the electronic configuration of $^2E_{2g}$ $[(a_{1g})^2(e_{2g})^3]$ is assigned to the ferrocenium ground state.[9] The E_{2g} state is split into two Kramers doublets. The smaller energy difference between the two Kramers doublets is the reason of the fast relaxation time and broad singlet ^{57}Fe-Moessbauer lines of most ferrocenium salts. Therefore, the splitting of the ^{57}Fe-Moessbauer line (about 0.6 mm s^{-1}) shows a larger energy difference between the two Kramers doublets in the ferrocenylruthenocenium$^{3+}(BF_4^-)_3$ salt, suggesting the presence of a kind of electronic effect of a ruthenocenium^{2+} cation on the Fe(III) atom in the ferrocenium$^+$ salt.

The results of the cyclic voltammography of ferrocenylruthenocene show a re-

Table 1. Q. S. and I. S. values of ferrocenylruthenocene and related compounds in the ^{57}Fe-Moessbauer spectra

Compounds	Temperature / K	Q. S. / mm s^{-1}	I. S. / mm s^{-1}
Biferrocene	78	2.33	0.53
Ferrocenylruthenocene	78	2.36	0.53
	300	2.29	0.42
Ferrocenylruthenocenium$^{3+}(BF_4^-)_3$	4.2	0.61	0.49
	78	0.59	0.45
	300	0.64	0.41
Ferrocenylruthenocenium$^+BF_4^-$	78	2.34	0.48
	190	2.33	0.47
	300	2.33	0.42
Ferrocenylruthenocenium$^+BF_4^-$[a]	78	2.32	0.48
		0.00	0.48
Ferrocenium$^+BF_4^-$	78	0.00	0.52
	300	0.00	0.40

a) Dispersed in poly(methylmethacrylate).

versible one-electron oxidation peak (E_{ox}; 0.45 V) and two irreversible one-electron oxidation peaks (E_{ox}; 0.85 and 0.92 V), as illustrated in Fig. 3-a. Based on the results of cyclic voltammography of ferrocene (E_{ox}; 0.44 V, as shown in Fig. 3-b) and ruthenocene (E_{ox}; 0,72 V) in the present study, the former value is ascribed to an oxidation of ferrocene-type iron atom and the latter one is to that of a ruthenocene-type ruthenium atom; i.e., Ru atoms are oxidized less easily than Fe atoms in ferrocenylruthenocene. Actually, ferrocene is oxidized by sulfuric acid and dichlorodicyanobenzoquinone, giving green ferrocenium solution, but ruthenocene itself is not oxidized by the same treatment.

While no peak is observed in ^{1}H- and ^{13}C-NMR spectra of ferrocenylruthenocenium$^+BF_4^-$ salt dissolved in acetonitrile probably because of paramagnetism of the monomeric cations, sharp signals are observed in ^{13}C-CP-MAS NMR spectra of the BF_4^- salt in solid state, indicating that the paramagnetism of ferrocenylruthenocenium cation should be quenched through an antiferromagnetic interaction by producing dimeric cations. The magnetic susceptibility study shows that the BF_4^- salt is diamagnetic at temperatures from 78 to 300 K. Figures 2-e and -f show the ^{57}Fe-Moessbauer spectra of the ferrocenylruthenocenium$^+BF_4^-$ salt, where only one kind of chemical state is observed for iron species and the Moessbauer parameters well correspond to those of ferrocenylruthenocene itself, indicating no possibility of monooxidation of ferrocenylruthenocene to its ferrocenium cation in solid.

Droege et al. already reported that oxidation of osmocene by $Ce(NH_4)_2(NO_3)_6$

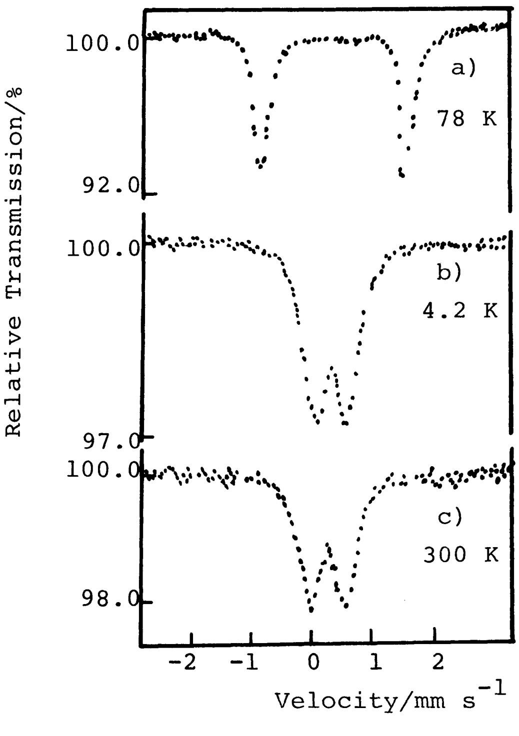

Fig. 1. ^{57}Fe-Moessbauer spectra of ferrocenylruthenocene (a) and ferrocenylruthenocenium$^{3+}(BF_4^-)_3$ salt (b,c) at indicated temperatures.

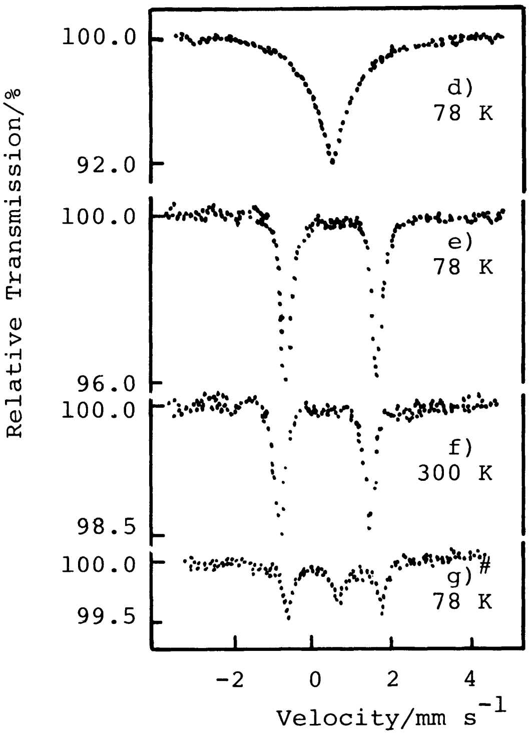

Fig. 2. ^{57}Fe-Moessbauer spectra of ferrocenium$^+BF_4^-$ (d) and ferrocenylruthenocenium$^+BF_4^-$ (e-g#) salts at indicated temperatures.

#; Dispersed in poly(methylmethacrylate) and NH_4PF_6 gave a diamagnetic $[Cp_2Os]_2^{2+}(PF_6^-)_2$ salt and they determined the crystal structure by X-ray analysis, concluding that two osmocenium cations are joined by an Os(III)-Os(III) bond, giving $[Cp_2Os\text{-}OsCp_2]^{2+}(PF_6^-)_2$. Based on the analogy to the PF_6^- salt of osmocene, it may be reasonable to assume that the reaction product with ferrocenylruthenocene and H_2SO_4-NH_4BF_4 is expressed as $[Cp(C_5H_4)Fe(II)Cp(C_5H_4)Ru(III)\text{-}Ru(III)(C_5H_4)CpFe(II)(C_5H_4)Cp]^{2+}(BF_4^-)_2$ with an antiferromagnetic chemical bond, Ru(III)-Ru(III), in the solid state, although the Ru-Ru bond may be unstable in solution probably because of dissociation of the dimer cation. In order to confirm this conclusion, ferrocenylruthenocenium$^+BF_4^-$ was dissolved in acetonitrile and dispersed in poly(methylmethacrylate). In the ^{57}Fe-Moessbauer spectrum, two kinds of iron atoms are observed; one is in Fe(II) and the other in Fe(III) state, as shown in Fig. 2-g$^{\#}$; i.e., the diamagnetic BF_4^- salt dissolves in acetonitrile, giving a paramagnetic $[Cp(C_5H_4)Fe(III)Cp(C_5H_4)Ru(II)]^+BF_4^-$ salt. Further studies must be conducted to provide direct evidence to prove the Ru(III)-Ru(III) bond in the BF_4^- salt by using ^{119}Ru-Moessbauer spectroscopy and other physicochemical measurements.

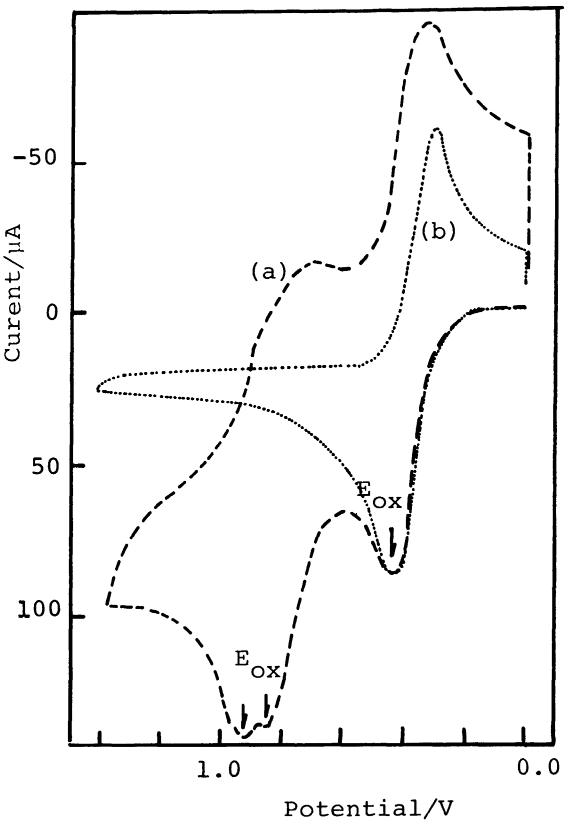

Fig. 3. Cyclic voltammogram of ferrocenylruthenocene (a) and ferrocene (b) in acetonitrile. (Sweep rate, 300 mV/s)

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