^{57}Fe-Mössbauer Spectroscopic Study of Ferrocenylruthenocene, [1](1,1′)Ferroceno[1](1,1′)ruthenocenophane, and Reaction Products with Some Oxidizing Agents

Masanobu WATANABE and Hirotoshi SANO*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukasawa, Setagaya-ku, Tokyo 158

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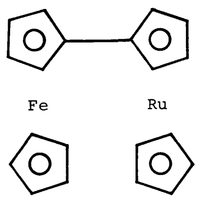
Ferrocenylruthenocene reacts with sulfuric acid–NH_4BF_4 to give a mono-oxidized diamagnetic ferrocenylruthenocenium BF_4^- salt, while it reacts with *p*-benzoquinon–$BF_3(Et_2O)$ to give a trioxidized paramagnetic ferrocenylruthenocenium $(BF_4^-)_3$ salt. Mössbauer parameters of the former salt are very similar to those of neutral ferrocenylruthenocene, suggesting that the structure of the salt is expressed as $[Cp(C_5H_4)Fe(II)(C_5H_4)CpRu(III)–Ru(III)Cp(C_5H_4)Fe(II)(C_5H_4)Cp]^{2+}(BF_4^-)_2$ with an antiferromagnetic Ru(III)–Ru(III) bond in the solid state. Well-dissolved quadrupole splitting (Q.S.) values observed for the latter salt (e.g., 0.61 mm s^{-1} at 4.2 K) suggest the presence of a kind of intramolecular electronic effect of a ruthenocenium moiety on the Fe(III) in the ferrocenium moiety.

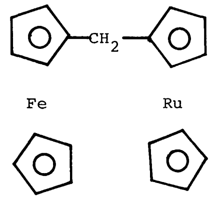
Although most ferrocene derivatives are oxidized by I_2 and $SuCl_4$, giving paramagnetic ferrocenium salts, ruthenocene reacts with the oxidizing agents, giving diamagnetic adducts determined as $[RuCp_2]–2I_2$ and $[RuCp_2]–1.5SnCl_4$ with Ru–I and Ru–Sn bonds, respectively, as found in the results of X-ray analysis or ^{129}I- and ^{119}Sn-Mössbauer spectroscopy.[1–3] Moreover, we have recently reported that ferrocenylruthenocene reacts with I_2, $HgCl_2$, and $SnCl_4$, giving diamagnetic adducts with Ru–I, Ru–Hg, Fe–Hg, and Ru–Sn bonds, respectively, based on the results of ^{57}Fe- and ^{119}Sn-Mössbauer and ^{13}C-CP-MAS NMR spectroscopies.[4–9] The results show that the ruthenocene moiety is a weaker Lewis base than the ferrocene moiety because of the 4d-electrons. There has been no report on the ferrocenylruthenocenium and [1]ferroceno[1]ruthenocenophanium salts, which have structures with well-separated ferrocence and ruthenocene moieties. The present study was planned to provide information about the chemical state of the iron atoms in the ferrocenylruthenocenium and [1]ferroceno[1]ruthenocenophanium cations by means of ^{57}Fe-Mössbauer spectroscopy and other physico-chemical measurements.

Experimental

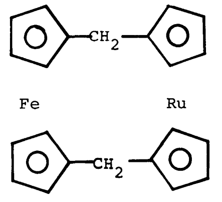
Materials: Ferrocenylruthenocene[10] and ferrocenylruthe-



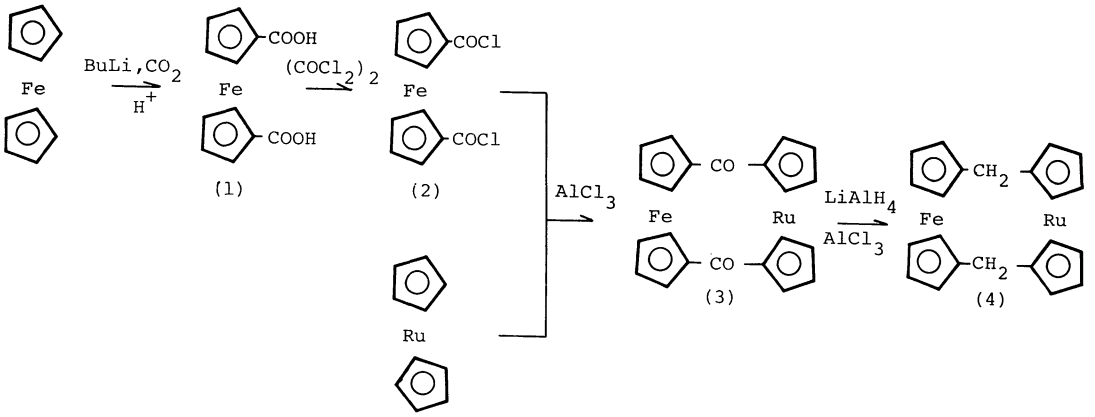
Ferrocenylruthenocene



Ferrocenylruthenocenyl-methane



[1]Ferroceno[1]ruthenoceno-phane



Scheme 1.

nocenylmethane[11] were prepared by the method described in previous reports.

[1]Ferroceno[1]ruthenocenophane-1,13-dione (**3**) was first prepared in the present study by the reaction of ruthenocene and 1.1′-bis(chloroformyl)ferrocene (**2**) prepared from 1.1′-ferrocene dicarboxylic acid (**1**), as shown in Scheme 1. A solution of ruthenocene (17.3 g, 0.075 mol) in CH_2Cl_2 (100 ml) was added to a solution of $AlCl_3$ (52 g) in CH_2Cl_2 (600 ml) at 0 °C and then a solution of (**2**) (23.3 g, 0.064 mol) in CH_2Cl_2 (200 ml) was added as in the case of preparation of [1.1]ferrocenophane-1,13-dione.[12] The crude products were separated by column chromatography on alumina. A purple-red band eluted by CH_2Cl_2–$CH_3COOC_2H_5$ (9:1) was determined to be the compound (**3**). Purple-red products were recrystallized from $CHCl_3$ (10.6 g, 30%). Found: C, 56.46; H, 3.60%. Calcd for $C_{22}H_{16}O_2FeRu$: C, 56.30: H, 3.44%. [1]Ferroceno[1]ruthenocenophane (**4**) was prepared by the following method. The compound (**3**) (4.7 g, 0.01 mol) was treated with $LiAlH_4$ (7.6 g, 0.2 mol) and $AlCl_3$ (26.8 g, 0.2 mol) in diethyl ether (400 ml). The mixture was diluted with water, filtered, and extracted with ether and hexane. The crude products were separated by column chromatography on alumina. The compound (**4**) was eluted as a yellow band by a mixture of hexane and benzene (1:1). The products were recrystallized from hexane mixed with benzene as yellow precipitates (4.1 g, yield; 92%). Found: C, 60.30; H, 4.82%. Calcd for $C_{22}H_{20}FeRu$: C, 59.87; H, 4.57%.

Ferrocenylruthenocene was treated with a stoichiometric amount of *p*-benzoquinone and BF_3–Et_2O in dry hexane mixed with benzene and gave dark brown products. The products were recrystallized from nitromethane mixed with ether and determined as ferrocenylruthenocenium $(BF_4^-)_3$. Found: C, 35.09; H, 3.33%. Calcd for $C_{20}H_{18}FeRuB_3F_{12}$: C, 35.55; H, 2.68%. Ferrocenylruthenocenium BF_4^- and PF_6^- salts 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 and cooled in ice. The cold solution was filtered and the filtrate added to a concentrated aqueous solution of NH_4BF_4 or NH_4PF_6. The solid formed was filtered and washed with H_2O and dried in vacuo over P_2O_5. Found: C, 48.80; H, 4.06%. Calcd for $C_{20}H_{18}FeRuBF_4$: C, 47.84; H, 3.61%. Found: C, 42.98; H, 3.33%. Calcd for $C_{20}H_{18}FeRuPF_6$: C, 42.87; H, 3.23%.

[1]Ferroceno[1]ruthenocenophane was treated with a stoichiometric amount of *p*-benzoquinone and BF_3–Et_2O in dry hexane mixed with benzene. It gave red-brown product, which was recrystallized from acetonitrile and determined as [1]ferroceno[1]ruthenocenophanium BF_4^-. Found: C, 50.68; H, 3.88%. Calcd for $C_{22}H_{20}FeRuBF_4$: C, 50.03; H, 3.82%. [1]Ferroceno[1]ruthenocenophanium PF_6^- and ferrocenylruthenocenylmethanium PF_6^- were prepared under the conditions used for the ferrocenylruthenocenium PF_6^- salt. Found: C, 44.86; H, 3.44%. Calcd for $C_{22}H_{20}FeRuPF_6$: C, 45.07; H, 3.44%. Found: C, 44.21; H, 3.45%. Calcd for $C_{21}H_{20}FeRuPF_6$: C, 43.91; H, 3.51%. [1]Ferroceno[1]ruthenocenophanium picrate salt was prepared by the reaction with a stoichiometric amount of *p*-benzoquinone and a large excess of picric acid in benzene. It gave yellow-green products, which were recrystallized from acetonitrile and determined as [1]ferroceno[1]ruthenocenophanium picrate. Found: N, 6.40; C, 50.75; H, 2.95%. Calcd for $C_{28}H_{22}O_7N_3FeRu$: N, 6.27; C, 50.24; H, 3.31%. [1]Ferroceno[1]ruthenocenophane-1,13-dione was treated with *p*-benzoquinone and BF_3–Et_2O under the conditions used for the [1]ferroceno[1]ruthenocenophanium BF_4^- salt and gave black products, which were recrystallized from acetonitrile and determined as 1,13-dioxo[1]ferroceno[1]ruthenocenophanium BF_4^-. Found: C, 47.91; H, 3.57%. Calcd for $C_{22}H_{18}O_2FeRuBF_4$: C, 47.51; H, 2.90%.

Measurements: ^{57}Fe-Mössbauer 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 ^{57}Fe was measured with respect to metallic iron and the experimental error of the I.S. and Q.S. values was estimated within ±0.02 mm s^{-1}. Cyclic voltammograms were obtained by using a Hokuto Denko HB-107A function generator and a Hokuto Denko HA-201 potentiostat combined with a standard three-elecrtrode configuration. A working electrode of platinum button (Beckman) and an Ag/AgCl reference electrode were connected via a salt bridge containing (0.1 mol dm^{-3}) $[(C_4H_9)_4N]ClO_4$ in CH_3CN.

Results and Discussion

Typical ^{57}Fe-Mössbauer parameters of ferrocenylruthenocene, [1]ferroceno[1]ruthenocenophane, and the related compounds are listed in Tables 1 and 2. [1]Ferroceno[1]ruthenocenophane-1,13-dione gives a relatively smaller Q.S. value (2.21 mm s^{-1}, at 78 K). This is probably because of the effect of electron attractive carbonyl groups attached to the cyclopentadienyl rings. The values of ferrocenylruthenocene (2.36 mm s^{-1} at 78 K) and [1]ferroceno[1]ruthenocenophane (2.41 mm s^{-1} at 78 K) correspond to the value of ferrocene itself (2.41 mm s^{-1} at 78 K), suggesting the absence of direct interaction between the Fe and Ru atoms in the neutral ferrocenylruthenocene and [1]ferroceno[1]ruthenocenophane.

Ferrocenylruthenocene is oxidized by *p*-benzoquinone–$BF_3(Et_2O)$ giving a paramagnetic ferrocenylruthenocenium $(BF_4^-)_3$ salt. The results of ^{57}Fe-Mössbauer study of the ferrocenylruthenocenium $(BF_4^-)_3$ salt show that well-resolved Q.S. values are observed at temperatures between 4.2 to 300 K, as shown in Fig. 1. The doublet is ascribed to a low-spin Fe(III) species. 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. 3-a). The magnetic susceptibility of the tricationic BF_4^- salt shows that the BF_4^- salt is paramagnetic at temperatures between 78—300 K; e.g., the effective magnetic moment is found to be 2.1 B.M. at 78 K, which is a little smaller than the value of normal ferrocenium salt (2.5 B.M. for ferrocenium BF_4^- salt). These facts suggest that the tricationic ferrocenylruthenocenium $(BF_4^-)_3$ salt is expressed as $[CpFe(III)(C_5H_4)(C_5H_4)Ru(IV)Cp]^{3+}(BF_4^-)_3$.

The results of ESR studies show that the electronic configuration $^2E_{2g}[(a_{1g})^2(e_{2g})^3]$ can be assigned to the ferrocenium ground state.[13] The E_{2g} state is split into

Table 1. ^{57}Fe-Mössbauer Parameters of Ferrocenylruthenocene and Related Compounds

Compound	Temp/K	Q.S./mm s^{-1}	I.S./mm s^{-1}	I(II)/I(III)[a]
Ferrocene	78	2.41	0.49	—
Ferrocenylruthenocene	78	2.36	0.53	—
	300	2.29	0.53	—
Ferrocenylruthenocenylmethane	78	2.44	0.53	—
Ferrocenylruthenocenium $(BF_4^-)_3$	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 PF_6^-	78	2.25	0.47	—
		0.34	0.47	0.32
	190	2.08	0.46	
		0.35	0.46	0.18
Ferrocenylruthenocenium BF_4^-[b]	78	2.32	0.48	
		0.00	0.48	2.44
Ferrocenylruthenocenylmethanium PF_6^-	78	2.21	0.48	
		0.00	0.49	0.64

a) I(II)/I(III) stands for the relative areal intensities of spectral components assigned to Fe(II) and Fe(III) state. b) Dispersed in poly(methyl methacrylate).

Table 2. ^{57}Fe-Mössbauer Parameters of [1]Ferroceno[1]ruthenocenophane and Related Compounds

Compound	Temp/K	Q.S./mm s^{-1}	I.S./mm s^{-1}	I(II)/I(III)[a]
[1]Ferroceno[1]ruthenocenophane	78	2.41	0.49	—
	300	2.40	0.45	—
[1]Ferroceno[1]ruthenocenophane-1,13-dione	78	2.21	0.51	—
	300	2.20	0.45	—
[1]Ferroceno[1]ruthenocenophanium BF_4^-	78	2.23	0.51	—
		0.32	0.47	1.96
	140	2.20	0.50	
		0.29	0.46	1.71
	190	2.21	0.48	
		0.30	0.44	1.09
	238	2.20	0.45	
		0.27	0.40	0.79
	300	2.21	0.44	
		0.27	0.38	0.54
[1]Ferroceno[1]ruthenocenophanium PF_6^-	78	2.33	0.47	
		0.00	0.46	0.31
	300	2.35	0.42	
		0.00	0.42	0.19
[1]Ferroceno[1]ruthenocenophanium picrate	78	2.22	0.45	
		0.00	0.46	6.18
	190	2.20	0.43	
		0.00	0.40	5.76
	300	2.20	0.40	
		0.00	0.42	4.95
1,13-Dioxo[1]ferroceno[1]ruthenocenophanium BF_4^-	78	2.17	0.46	
		0.34	0.45	0.38
	190	2.17	0.44	
		0.33	0.42	0.32
	300	2.13	0.42	
		0.29	0.40	0.21

a) I(II)/I(III) stands for the relative areal intensities of spectral components assigned to Fe(II) and Fe(III) state.

two Kramers doublets. A negligibly small energy difference between the two Kramers doublets is known to be the reason for the fast relaxation time and for the broad singlet in ^{57}Fe-Mössbauer spectra of most ferrocenium salts. Therefore, the splitting of the ^{57}Fe-Mössbauer line (about 0.6 mm s^{-1}) and the smaller magnetic moments found in the ferrocenylruthenocenium $(BF_4^-)_3$ salt imply a larger energy difference between the two Kramers doublets in the ferrocenylruthenocenium $(BF_4^-)_3$ salt. This suggests the

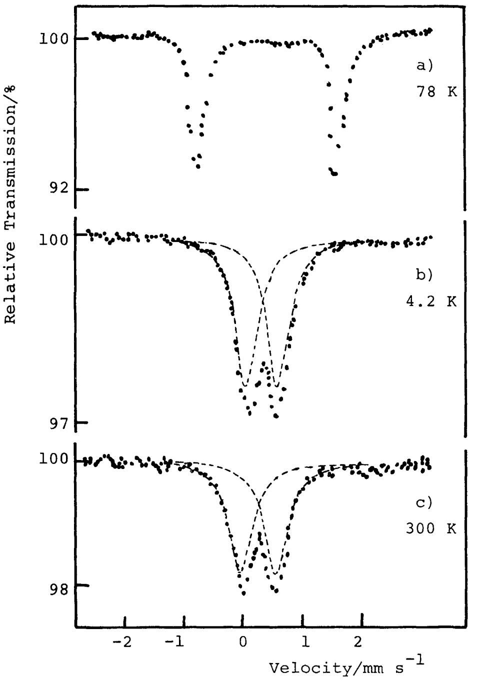


Fig. 1. ^{57}Fe-Mössbauer spectra of ferrocenylruthenocene (a) and tricationic ferrocenylruthenocenium $(BF_4^-)_3$ salt (b,c), at indicated temperatures.

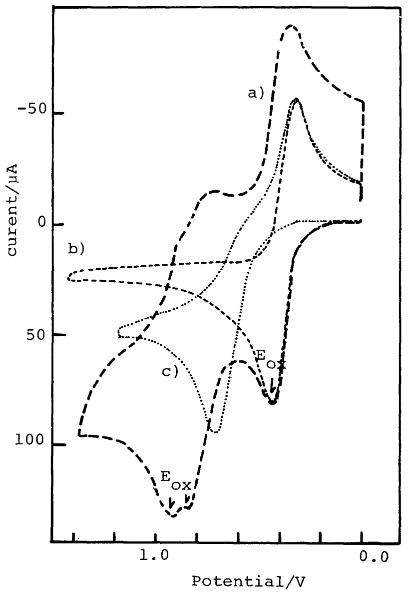


Fig. 2. Cyclic voltammograms of ferrocenylruthenocene (a), ferrocene (b), and ruthenocene (c) in acetonitrile. (Sweep rate; 300 mV s^{-1}).

presence of some kind of electronic effect of a ruthenocenium moiety on the Fe(III) ion in the ferrocenium moiety. The tricationic BF_4^- salt is so unstable that high spin Fe(II) species are observed in the Mössbauer spectroscopic measurement when the salt stands at room temperature for a few days.

The results of the cyclic voltammography of ferrocenylruthenocene show a reversible 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. 2. Based on the results of cyclic voltammography of ferrocene (E_{OX}; 0.44 V) and ruthenocene (E_{OX}; 0.72 V), the former value (0.45 V) can be ascribed to an oxidation of a ferrocene-type iron atom and the latter (0.85 and 0.92 V) to that of a ruthenocene-type ruthenium atom. This indicates that Ru atom is less easily oxidized than the Fe atom in ferrocenylruthenocene. Actually ferrocene is oxidized in sulfuric acid and dichlorodicyanobenzoquinone, giving the green ferrocenium salt, but ruthenocene is not oxidized by the same treatment.

Ferrocenylruthenocene is mono-oxidized in sulfuric acid, giving a green-colored solution characteristic of ferrocenium salts. Addition of a concentrated aqueous solution of NH_4BF_4 to the green colored solution gives red-brown precipitates determined as ferrocenylruthenocenium BF_4^-. No peak is observed in ^1H and ^{13}C NMR spectra of ferrocenylruthenocenium BF_4^- salt dissolved in acetonitrile probably because of the paramagnetism of the monomeric cations, but sharp signals are observed in ^{13}C-CP-MAS NMR spectra of the BF_4^- salt in the solid state. This indicates that the paramagnetism of monomeric 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 3-b and -c show the ^{57}Fe-Mössbauer spectra of the ferrocenylruthenocenium BF_4^- salt, where only one kind of chemical state is observed for the iron species and the Mössbauer parameters correspond well to those of ferrocenylruthenocene itself. The absence of either a broad singlet line or an anomalously larger Q.S. line than that of ferrocenylruthenocene indicates that the ferrocene moiety of the ferrocenylruthenocenium is neither oxidized to ferrocenium nor bound with an Fe–Fe bonding as described in $[(C_5H_4)CpRu(C_5H_4)CpFe\text{–}FeCp(C_5H_4)RuCp(C_5H_4)]^{2+}$ in a solid. However, the BF_4^- salt is so unstable in solution that the diamagnetic BF_4^- salt dissolves in acetonitrile changing into a paramagnetic ferrocenium salt. This suggests the dissociation of the dimeric BF_4^- salt to a monomeric ferrocenylruthenocenium salt in solution.

Ferrocenylruthenocene is oxidized in sulfuric acid containing NH_4PF_6, giving deep purple precipitates determined as ferrocenylruthenocenium PF_6^-. In contrast with the diamagnetic BF_4^- salt, the PF_6^- salt is paramagnetic from 78 K to 300 K. The effective magnetic moment of the PF_6^- salt is found to be 2.0 BM at 300 K which is smaller than the value of normal ferrocenium salts. In the spectrum of the PF_6^- salt measured at 78 K, two kinds of chemical states of iron species are observed, as shown in Table 1 and Fig. 4(a—c). The component with a smaller Q.S. value

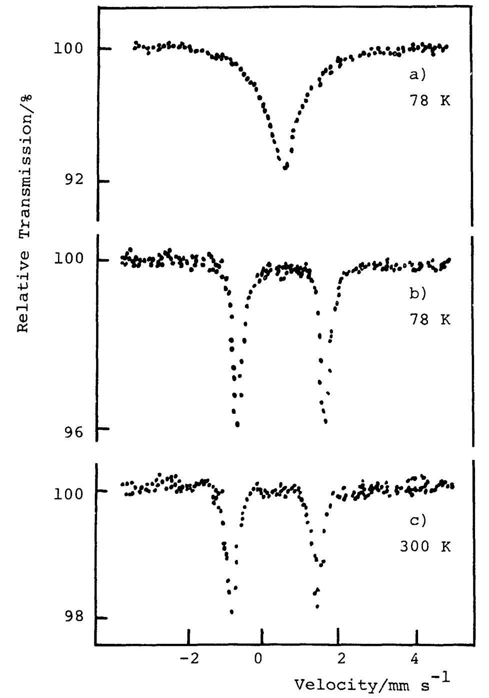


Fig. 3. ^{57}Fe-Mössbauer spectra of ferrocenium BF_4^- (a) and ferrocenylruthenocenium BF_4^- (b,c) salts, at indicated temperatures.

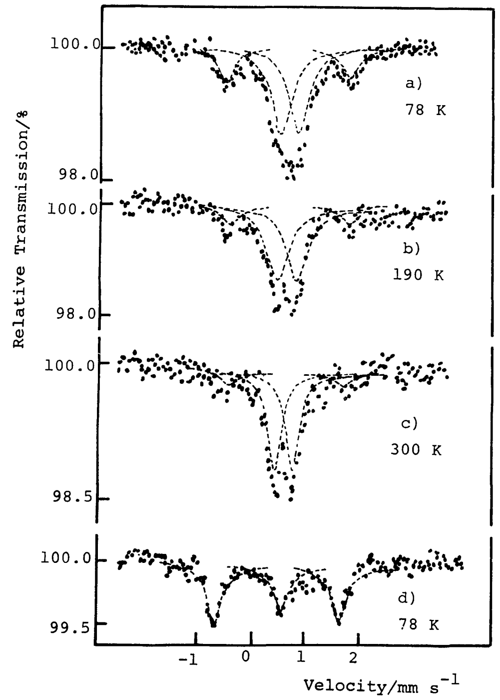


Fig. 4. ^{57}Fe-Mössbauer spectra of ferrocenylruthenocenium PF_6^- (a—c) salt and ferrocenylruthenocenium BF_4^- salt in poly(methyl methacrylate) (d), at indicated temperatures.

(2.25 mm s^{-1}) than the value of neutral ferrocene is ascribed to a low-spin Fe(II) species and the other component with a small Q.S. value (0.34 mm s^{-1}) to a low-spin Fe(III) species, although all the mononuclear ferrocene and ferrocenium derivatives are known to show only a single spectral component in their spectra. Moreover, areal intensity of the Fe(III) is much larger than that of Fe(II). The facts indicate that a large portion of ferrocene moiety (more than 77% at 78 K) of the ferrocenylruthenocene is oxidized into ferrocenium in the ferrocenylruthenocenium PF_6^-.

All the results obtained in the present study suggest that the difference of Mössbauer and magnetic properties of the ferrocenylruthenocenium BF_4^- salt from those of the PF_6^- salt in the solid state could not be interpreted in terms of an intramolecular effect in a monomeric cation. However they could be interpreted by assuming an intermolecular effect such as formation of dimeric cations. In order to confirm this conclusion, ferrocenylruthenocenium BF_4^- was dissolved in acetonitrile and dispersed in poly(methyl methacrylate). In the Mössbauer spectrum of the salt measured at 78 K, two kinds of iron atoms were observed; one is in an Fe(II) state and the other is in an Fe(III) state, as shown in Fig. 4-d. This Mössbauer spectrum is very different from that of the dimeric BF_4^- salt in a solid (shown in Fig. 3-b,c) and similar to that of ferrocenylruthenocenium PF_6^-, except for the areal intensities of spectral components assigned to Fe(II) and Fe(III). Based on the fact that ferrocenylruthenocene is not oxidized in acetonitrile with poly(methyl methacrylate), it can be concluded that dissociation of the dimeric BF_4^- salt gives a monomeric ferrocenylruthenocenium BF_4^- salt in the solution.

Droege et al. already reported that oxidation of osmocene by $Ce(NH_4)_2(NO_3)_6$ and NH_4PF_6 gives a diamagnetic $[Cp_2Os]_2(PF_6)_2$ salt and determined the crystal structure by using X-ray diffraction, concluding that the two osmocenium cations are jointed by an Os(III)–Os(III) bond; $[Cp_2Os\text{–}OsCp_2]^{2+}(PF_6^-)_2$.[14] Based on the analogy to the dimeric osmocenium PF_6^- salt and the absence of an Fe–Fe bond in the ferrocenylruthenocenium BF_4^- salt, it may be reasonable to assume that the reaction product of ferrocenylruthenocene with $H_2SO_4\text{–}NH_4BF_4$ is expressed as $[Cp(C_5H_4)\text{-}Fe(II)Cp(C_5H_4)Ru(III)\text{–}Ru(III)(C_5H_4)CpFe(II)(C_5H_4)\text{-}Cp]^{2+}(BF_4^-)_2$ with a Ru(III)–Ru(III) bond in a solid, although the metal–metal chemical bond may be unstable in solution probably because of dissociation of the dimer cation; i.e., the dimeric BF_4^- diamagnetic cation dissolves in acetonitrile, giving a monomeric $[Cp(C_5H_4)Fe(III)Cp(C_5H_4)Ru(II)]^+BF_4^-$ paramagnetic cation. On the other hand, ferrocenylruthenocenium PF_6^- salt can be expressed as $[Cp(C_5H_4)Fe(III)Cp\text{-}(C_5H_4)Ru(II)]^+PF_6^-$ including a small amount of $[Cp(C_5H_4)Fe(II)Cp(C_5H_4)Ru(III)\text{–}Ru(III)(C_5H_4)CpFe\text{-}(II)(C_5H_4)Cp]^{2+}(PF_6^-)_2$. This assumes that the antiferromagnetic Ru(III)–Ru(III) bond in the PF_6^- salt is not as stable as in the BF_4^- salt.

All attempts to prepare $[Cp_2Ru(III)\text{–}Ru(III)Cp_2]^{2+}$

cation by means of chemical and electrochemical oxidation of ruthenocene have been unsucessful, probably because of the instability of the Cp_2Ru^+ cation. Based on the results of electrochemical studies, it is known that osmocene is oxidized in two one-electron steps ($E_{1/2}$, 0.75 and 1.37 V), while ruthenocene in a two-electron step ($E_{1/2}$, 0.78 V).[15,16] The ruthenocene moiety of ferrocenylruthenocene is found to be oxidized in two one-electron steps (E_{OX}, 0.85 and 0.92 V), associated with an antiferromagnetic bond formation, Ru(III)–Ru(III).

[1]Ferroceno[1]ruthenocenophane was prepared in the present study by reduction of [1]ferroceno[1]-ruthenocenophane-1,13-dione, as shown in Scheme 1, in order to improve the poor yield in Westerhoff's method.[17] Studies of the cyclic voltammography of [1]ferroceno[1]ruthenocenophane show a reversible one-electron oxidation peak (E_{OX}; 0.39 V) and an irreversible two-electron oxidation peak (E_{OX}; 0.89 V). The former value (0.39 V) is ascribed to the oxidation of ferrocene-type Fe atoms and the latter (0.89 V) to that of ruthenocene-type Ru atoms.

[1]Ferroceno[1]ruthenocenophane is easily oxidized by *p*-benzoquinone–$BF_3(Et_2O)$ in benzene, giving a paramagnetic dark brown [1]ferroceno[1]ruthenocenophanium BF_4^- salt. The effective magnetic moments of the BF_4^- salt is found to be 2.0 BM at 300 K. This value corresponds well with the value for the ferrocenylruthenocenium PF_6^- salt (2.0 BM at 300 K). ^{57}Fe-Mössbauer spectroscopic studies of [1]ferroceno-[1]ruthenocenophanium BF_4^- salt show that two chemical states of the iron species are observed, as shown in Table 2 and Fig. 5. The component with a little smaller Q.S. value (2.23 mm s^{-1}) than the value of neutral metallocene is ascribed to a low-spin Fe(II) species and the other component with a small Q.S. value (0.32 mm s^{-1}) to a low-spin Fe(III) species. Moreover, the decreased intensity in the large Q.S. component and the increased intensity in the small Q.S. component are observed with increasing temperature. I(II) and I(III) in Tables 1 and 2 stand for the relative areal intensities of the spectral components assigned to the Fe(II) and Fe(III) state respectively. The intensity ratio, I(II)/I(III), in [1]ferroceno[1]-ruthenocenophanium BF_4^- is found to be 1.96 and 0.54 at 78 and 300 K, respectively. The temperature dependence of the intensity ratio of I(II)/I(III) is much larger than those found in a number of mixed-valence (trapped-valence type) biferrocene derivatives. This indicates that the large temperature dependence of the areal intensities of the Fe(II) and Fe(III) state in the [1]ferroceno[1]ruthenocenophanium BF_4^- salt cannot be ascribed to the difference in the recoil-free fraction of the iron atoms in the molecule.

Based on the results of ferrocenylruthenocenium BF_4^- and PF_6^-, it is reasonable to assume that the [1]ferroceno[1]ruthenocenophanium BF_4^- salt has an antiferromagnetic Ru(III)–Ru(III) bond at lower temperatures, although the Ru–Ru bond is more unstable than that of ferrocenylruthenocenium BF_4^- salt. This is probably because of steric hindrance in the [1]ferroceno[1]ruthenocenophanium salt. It is found that the Ru(III)–Ru(III) bond in the dimeric BF_4^- salt dissociates easily at higher temperatures giving a monomeric $[(C_5H_4)_2Fe(III)(CH_2)_2(C_5H_4)_2Ru(II)]^+BF_4^-$ salt. Therefore, it is concluded that the [1]ferroceno-[1]ruthenocenophanium BF_4^- salt is expressed as $[(C_5H_4)_2Fe(II)(CH_2)_2(C_5H_4)_2Ru(III)\text{–}Ru(III)(C_5H_4)_2(CH_2)_2Fe(II)(C_5H_4)_2]^{2+}(BF_4^-)_2$ including a small amount of $[(C_5H_4)_2Fe(III)(CH_2)_2(C_5H_4)_2Ru(II)]^+BF_4^-$ in the solid at low temperatures.

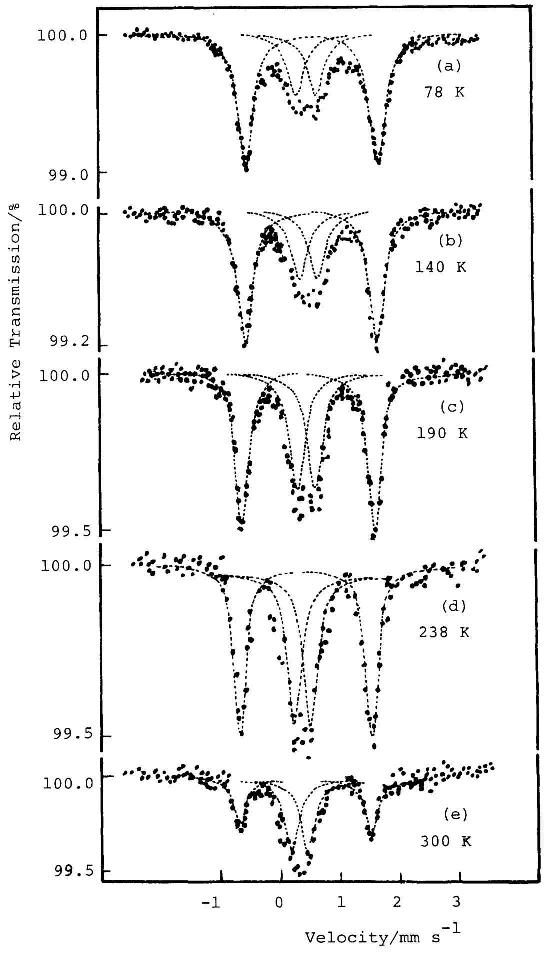


Fig. 5. ^{57}Fe-Mössbauer spectra of [1]ferroceno[1]-ruthenocenophanium BF_4^- salt, at indicated temperatures.

[1]Ferroceno[1]ruthenocenophane is also oxidized by *p*-benzoquinone–picric acid in benzene, giving a paramagnetic green-yellow [1]ferroceno[1]ruthenocenophanium picrate salt. The effective magnetic moments of the picrate salt is found to be 1.6 BM at 300 K, which is much smaller than the value of normal ferrocenium salts (2.4—2.6 BM). A ferrocene-type Mössbauer line component (Q.S. 2.22 mm s^{-1} at 78 K) with a small

amount of ferrocenium-type Mössbauer line component is observed in the Mössbauer spectra of the picrate salt, as shown in Fig. 6-a and -b, although the temperature dependence of the intensity ratio is much smaller than that of the BF_4^- salt. The facts indicate that an antiferromagnetic Ru(III)–Ru(III) bond is more stable in the picrate than in the BF_4^- salt. The picrate salt is expressed as $[(C_5H_4)_2Fe(II)(CH_2)_2(C_5H_4)_2Ru(III)–Ru(III)(C_5H_4)_2(CH_2)_2(C_5H_4)_2Fe(II)]^{2+}$ (picrate)$_2$ including a small amount of $[(C_5H_4)_2Fe(III)(CH_2)_2(C_5H_4)_2Ru(II)]^+$ picrate, as in the case of the BF_4^- salt.

Contrary to the picrate salt, [1]ferroceno[1]ruthenocenophanium PF_6^- salt gives ferrocenium type Mössbauer lines with a small portion of ferrocene type's line component, as shown in Fig. 6-c and -d. The fact that the Mössbauer spectroscopic features of the [1]ferroceno[1]ruthenocenophanium PF_6^- salt are similar to those of the ferrocenylruthenocenium PF_6^- suggests that the antiferromagnetic Ru(III)–Ru(III) bond is unstable in the [1]ferroceno[1]ruthenocenophanium PF_6^- salt. The PF_6^- salt is expressed as $[(C_5H_4)_2Fe(III)(CH_2)_2(C_5H_4)_2Ru(II)]^+PF_6^-$ including a small amount of $[(C_5H_4)_2Fe(II)(CH_2)_2(C_5H_4)_2Ru(III)–Ru(III)(C_5H_4)_2(CH_2)_2(C_5H_4)_2Fe(II)]^{2+}$ $(PF_6^-)_2$.

[1]Ferroceno[1]ruthenocenophane-1,13-dione was first prepared in the present study. The cyclic voltammography of the [1]ferroceno[1]ruthenocenophane-1,13-dione shows a reversible one-electron oxidation peak (E_{OX}; 0.92 V, assigned to ferrocene moiety) and an irreversible two-electron oxidation peak (1.21 V, assigned to ruthenocene moiety). The much higher values than those of ferrocenylruthenocene and [1]ferroceno[1]ruthenocenophane are ascribed to the effect of an electron-attractive carbonyl groups. [1]Ferroceno[1]ruthenocenophane-1,13-dione is oxidized by *p*-benzoquinone and BF_3–Et_2O as in the case of ferrocenylruthenocenium BF_4^-, giving a paramagnetic (effective magnetic moment, 2.1 BM at 300 K) dark brown 1,13-dioxo[1]ferroceno[1]ruthenocenophanium BF_4^- salt. The two types of iron atoms (Q.S.; 2.17 mm s^{-1}, assigned to Fe(II) and 0.34 mm s^{-1} to Fe(III) species, both at 78 K) are observed. The much larger areal intensity of the Fe(III) component than that of Fe(II) suggests that the antiferromagnetic Ru(III)–Ru(III) bond is unstable in the BF_4^- salt, probably because of the effect of electron attractive carbonyl groups on the e_{2g} electrons of the Ru atom. The BF_4^- salt is expressed as $[(C_5H_4)_2Fe(III)(CO)_2$-

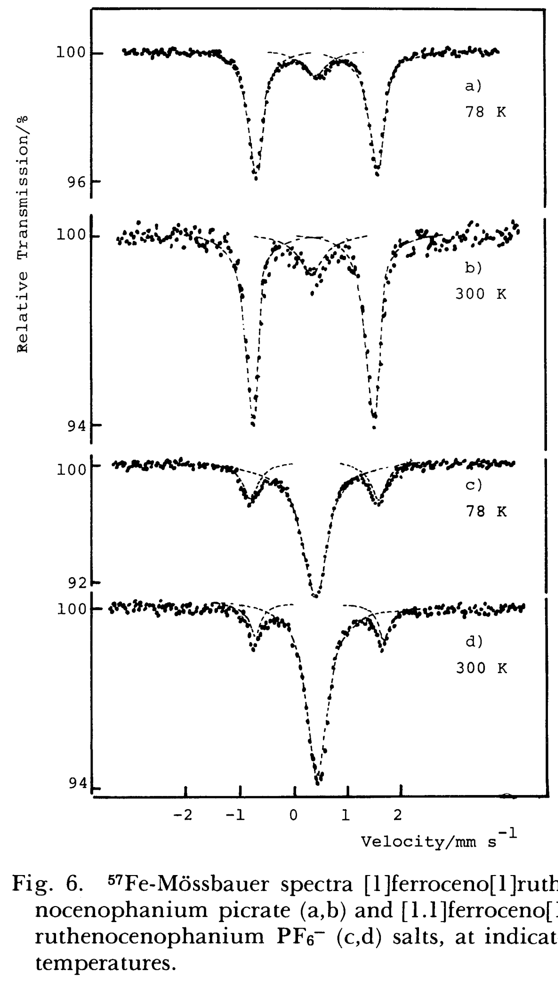


Fig. 6. ^{57}Fe-Mössbauer spectra [1]ferroceno[1]ruthenocenophanium picrate (a,b) and [1.1]ferroceno[1]ruthenocenophanium PF_6^- (c,d) salts, at indicated temperatures.

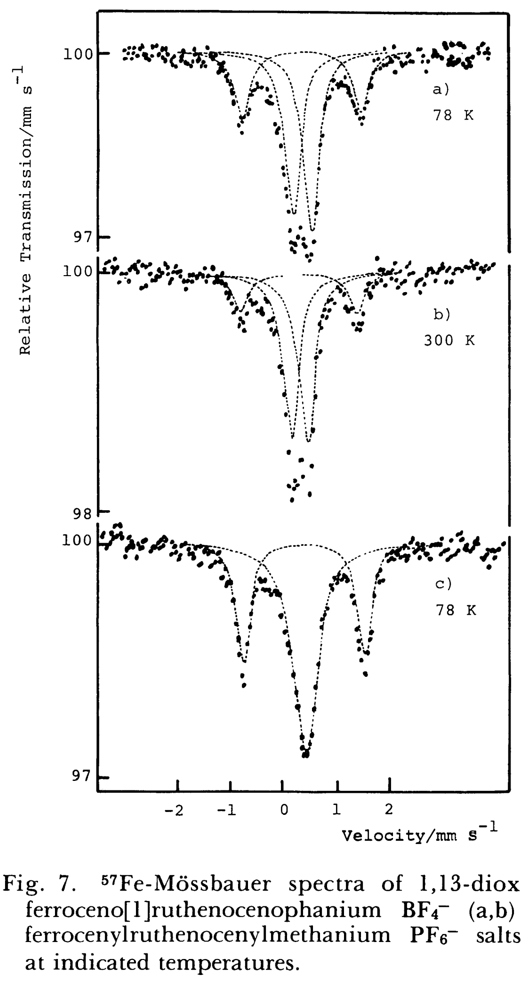


Fig. 7. ^{57}Fe-Mössbauer spectra of 1,13-dioxo[1]ferroceno[1]ruthenocenophanium BF_4^- (a,b) and ferrocenylruthenocenylmethanium PF_6^- salts (c), at indicated temperatures.

$(C_5H_4)_2Ru(II)]^+BF_4^-$ including a small amount of $[(C_5H_4)_2Fe(II)(CO)_2(C_5H_4)_2Ru(III)$–$Ru(III)(C_5H_4)_2$-$(CO)_2(C_5H_4)_2Fe(II)]^{2+}(BF_4^-)_2$.

The ferrocene moiety is so separated from a ruthenocene moiety in a ferrocenylruthenocenylmethane molecule compared in ferrocenylruthenocene that the Fe and Ru atoms cannot directly interact with each other. Ferrocenylruthenocenylmethane reacts with sulfuric acid containing NH_4PF_6, giving a monocationic ferrocenylruthenocenylmethanium PF_6^- salt. In the Mössbauer spectrum of the salt, two types of iron atoms (Q.S., 2.21 mm s^{-1}, ascribed to ferrocene type and 0.0 mm s^{-1}, to ferrocenium type) are observed, as seem in Fig. 7-c. Because there is no possibility of an intramolecular electron-transfer process between the Ru and Fe atoms, the presence of Fe(II) component in the PF_6^- salt suggests the Ru(III)–Ru(III) bond formation in the salt, although the Ru(III)–Ru(III) bond may not be as stables as that of ferrocenylruthenocenium BF_4^-.

All the results obtained in the present studies support the relatively stable chemical-bond formation between the Ru(III) and Ru(III) atoms in ferrocenylruthenocenium BF_4^- and [1]ferroceno[1]ruthenocenophanium picrate salt. Further studies must be conducted to provide direct evidence to prove the Ru(III)–Ru(III) coordination bond in the salts by using ^{99}Ru Mössbauer spectroscopy and/or single crystal X-ray analysis.

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