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Mössbauer Spectroscopic Studies of Mercury(II) Chloride Adducts with Binuclear Metallocenes

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Biferrocene and ferrocenylruthenocene react with $HgCl_2$ to give very stable adducts. Large quadrupole splitting values (2.93 mm s^{-1} for biferrocene-$2HgCl_2$ and 2.99 mm s^{-1} for ferrocenylruthenocene-$5HgCl_2$, both at 78 K) indicate the presence of a direct interaction between the Fe and Hg atoms. The stabilities of their adducts suggest a chelating effect between the Fe and Fe or Fe and Ru atoms in biferrocene or ferrocenylruthenocene, respectively.

All attempts in preparing a stable adduct of mononuclear ferrocene with a Lewis acid such as Hg^{2+}, Sn^{4+}, and I^+ have been unsuccessful, whereas a number of the corresponding ruthenocene adducts were reported to be very stable.[1–4]

It was recently shown in our previous reports that [2]ferrocenophane derivatives react with various Lewis acids such as Sn^{4+}, Hg^{2+}, and I^+ to give stable adducts containing a chemical bond between the Fe and Lewis acid atoms.[5–7] The stabilities of [2]ferrocenophane adducts were ascribed to the distorted structure of [2]ferrocenophane which makes the nonbonding e_{2g} electrons of the iron atom in ferrocene easier to be ligated to a Lewis acid atom.

The other category of ferrocene derivatives which can provide a stable adduct with a Lewis acid, may be expected in binuclear metallocene derivatives, because their adducts with a Lewis acid are stabilized by a chelating effect of the binuclear ferrocene derivatives if they have a suitable molecular structure.[8] Fortunately, a number of binuclear ferrocene derivatives have been synthesized and reported in connection with studies of the mixed-valence state of iron atoms in their monocation salts. For instance, biferrocenium triiodide shows a so-called trapped valence state, while biferrocenylenium pentaiodide shows an averaged valence state.[9–11] It is also expected that ferrocenylruthenocene derivatives can provide much more stable adducts with a Lewis acid than the binuclear ferrocenes and that the electronic state of iron atoms in the adducts may provide information about the chelating effect.

Experimental

Materials. Biferrocene,[12] biferrocenylene,[13] diferrocenylmethane and diferrocenylethane,[14] 1,12-dimethyl[1.1]ferrocenophane,[15] [2.2]ferrocenophane,[16] ferrocenylruthenocene,[17] and ferrocenylruthenocenylmethane[18] were prepared by the methods reported previously.

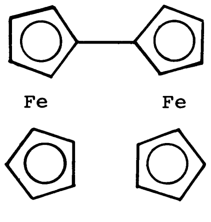
Adducts of diferrocenylmethane, 1,2-diferrocenylethane, ferrocenylruthenocene and ferrocenylruthenocenylmethane with $HgCl_2$ were prepared in diethyl ether by a similar method to that used in the case of biferrocene-$2HgCl_2$ adduct.[8] Found: C, 25.71; H, 2.71%. Calcd for biferrocene-$2HgCl_2$, $C_{20}H_{18}Fe_2Hg_2Cl_4$: C, 26.29; H, 1.97%. Found: C, 12.52; H, 0.99; Fe, 5.54%. Calcd for diferrocenylmethane-$6HgCl_2$, $C_{21}H_{20}Fe_2Hg_6Cl_{12}$: C, 12.99; H, 1.10; Fe, 4.78%. Found: C, 13.02; H, 1.09; Fe, 5.51%. Calcd for 1,2-diferrocenylethane-$6HgCl_2$, $C_{22}H_{22}Fe_2Hg_6Cl_{12}$: C, 13.05; H, 1.10; Fe, 5.08%. Found: C, 14.17; H, 1.27%. Calcd for ferrocenylruthenocene-$5HgCl_2$, $C_{20}H_{18}FeRuHg_5Cl_{10}$: C, 13.55; H, 1.03%. Found: C, 22.96; H, 2.02%. Calcd for ferrocenylruthenocenylmethane-$2.5HgCl_2$, $C_{21}H_{20}FeRuHg_{2.5}Cl_5$: C, 22.75; H, 1.82%.

Reaction products of biferrocenylene, 1,12-dimethyl[1.1]ferrocenophane and [2.2]ferrocenophane were prepared in ethanol instead of diethyl ether because of better solubility, by following a method similar to that used for the biferrocene-$2HgCl_2$ adduct. The dark green precipitates that formed were filtered, washed with ethanol or diethyl ether and dried in a vacuum. Found: C, 16.86; H, 1.13; Hg, 54.00%. Calcd for biferrocenylenium$(HgCl_3^-)(HgCl_2)_3$, $C_{20}H_{16}Fe_2Hg_4Cl_9$; C, 16.11; H, 1.07; Hg, 53.86%. Found: C, 20.51; H, 1.71%. Calcd for 1,12-dimethyl[1.1]ferrocenophanium$(HgCl_3^-)(HgCl_2)_{2.5}$, $C_{24}H_{24}Fe_2Hg_{3.5}Cl_8$: C, 20.65; H, 1.70%. Found: C, 27.74; H, 2.31%. Calcd for [2.2]ferrocenophanium$^{2+}(HgCl_3^-)_2$, $C_{24}H_{24}Fe_2Hg_2Cl_6$: C, 27.26; H, 2.37%.

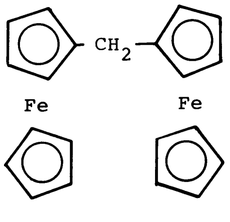
Measurements. ^{57}Fe-Mössbauer measurements were carried out using a ^{57}Co(Pt) source moving in a constant acceleraion mode. The values of the isomer shifts were described with respect to metallic iron foil. The experimental error of the isomer shifts (I.S.) and quadrupole splittings (Q.S.) was ±0.02 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-electrode 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

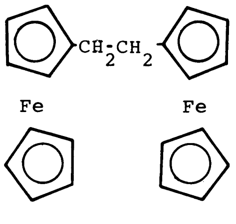
Biferrocene reacts with a large excess of $HgCl_2$ in diethyl ether, giving deep-red precipitates thought to be biferrocene-$2HgCl_2$, based on an elemental analysis. The adduct is stable in air for a long time (more than 200 d) at room temperature, while ferrocene-$7HgCl_2$ changes immediately into a ferricinium salt.[19] Other biferrocene derivatives, such as



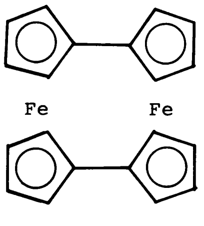
biferrocene



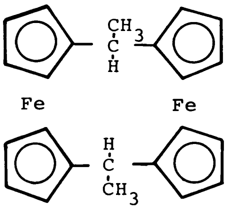
diferrocenylmethane



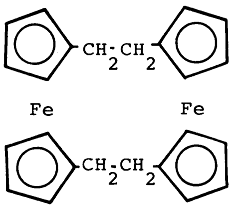
1,2-diferrocenylethane



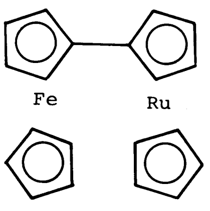
biferrocenylene



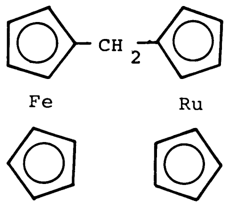
1,12-dimethyl[1.1]-ferrocenophane



[2.2]ferrocenophane



ferrocenylruthenocene



ferrocenylruthenocenylmethane

1′,1‴-dihalobiferrocene 1′,1‴-dialkylbiferrocene, react with $HgCl_2$ to give paramagnetic green precipitates. The results of Mössbauer spectroscopic studies of these precipitates show that these biferrocene are oxidized by $HgCl_2$, probably because of a steric hindrance of the substituents and that they give a trapped-valence state for each monocationic ferricinium salt.

Typical Mössbauer spectra of a biferrocene–$2HgCl_2$ adduct and the biferrocene itself, are shown in Fig. 1 and Mössbaur parameters are listed in Table 1. The Q.S. value (2.93 mm s^{-1} at 78 K) found in the biferrocene–$2HgCl_2$ adduct is a little smaller than that of [2]ferrocenophane–$3HgCl_2$ adduct (3.29 mm s^{-1} at 78 K)[6] but still larger than that of the original biferrocene. The results indicate that the biferrocene–$2HgCl_2$ adduct should have Fe–Hg bonds, as already verified in the $HgCl_2$ or $SnCl_4$ adducts of [2]ferrocenophane.[5,6]

A little lower Q.S. value and large stability of the

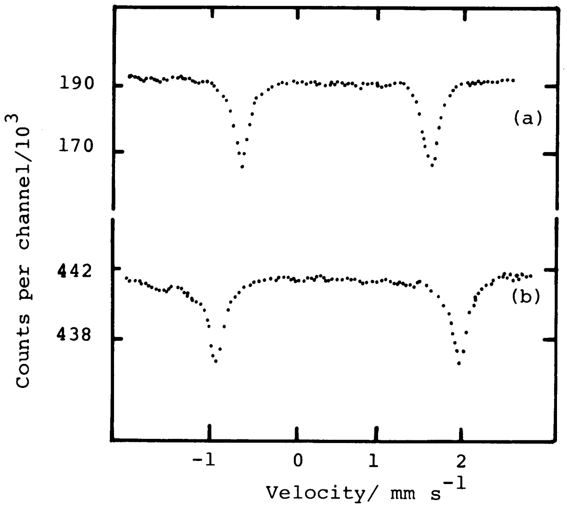


Fig. 1. Mössbauer spectra of (a) biferrocene and (b) biferrocene–$2HgCl_2$ adduct, both at 78 K.

Table 1. Mössbauer Parameters of Binuclear Ferrocene Derivatives and Their $HgCl_2$ Adducts and Salts

Compound	Temperature K	Q.S. mm s^{-1}	I.S. mm s^{-1}
Biferrocene	78	2.33	0.53
Diferrocenylmethane	78	2.38	0.52
Diferrocenylethane	78	2.40	0.50
Biferrocenylene	78	2.44	0.53
1,12-Dimethyl[1.1]-ferrocenophane	78	2.45	0.54
[2.2]Ferrocenophane	78	2.43	0.52
Ferrocenylruthenocene	78	2.36	0.53
	300	2.29	0.46
Biferrocene–$2HgCl_2$	78	2.93	0.55
Diferrocenylmethane–$6HgCl_2$	78	3.02	0.53
Diferrocenylethane–$6HgCl_2$	78	3.00	0.50
Biferrocenylenium$^+$ $HgCl_3^-(HgCl_2)_3$	78	1.87	0.53
	200	1.83	0.47
	300	1.76	0.43
1,12-Dimethyl[1.1]ferrocenophanium$^+$ $HgCl_3^-(HgCl_2)_{2.5}$	78	1.93	0.52
		0.0	0.53
[2.2]ferrocenophanium^{2+}-$(HgCl_3^-)_2$	78	0.0	0.53
Ferrocenylruthenocene–$5HgCl_2$	78	2.99	0.57
Ferrocenylruthenocenylmethane–$2.5HgCl_2$	78	2.84	0.55
Biferrocenylenium$^+$ I_5^- [a]	4.2	1.756	0.542
	300	1.719	0.441
Ferrocene–$7HgCl_2$[b]	275	2.94	0.45

a) Data were taken from Ref. 10. b) Data were taken for the fresh sample reported in Ref. 19.

biferrocene–$2HgCl_2$ adduct compared with ferrocene–$7HgCl_2$[19] suggest that biferrocene reacts with $HgCl_2$ as a chelating agent.

It is found that biferrocene reacts with $SnCl_4$ to give only green-colored precipitates in which iron atoms are not ligated to Sn^{4+} ions but partially oxidized to a mixed-valence state (Q.S. values, 2.26 and 0.29 mm s^{-1} at 78 K).[20] Also, biferrocene is oxidized to a dicationic biferricinium salt in the reaction with $SbCl_5$ (Q.S., 0.25 mm s^{-1} and I.S., 0.55 mm s^{-1} at 78 K, which are characteristic of ferricinium-like iron(III)). Although [2]ferrocenophane reacts with other Lewis acid species, such as $CdCl_2$, $ZnCl_2$, $CoCl_2$, to give corresponding adducts with them,[21] biferrocene does not react with these Lewis acids. The results may be interpreted by assuming that Hg^{2+} ions are a softer acid than Sn^{4+} and Sb^{5+} atoms, and that the e_{2g} electrons in biferrocene cannot be ligated to Lewis acids harder than Hg^{2+}.

Diferrocenylmethane and 1,2-diferrocenylethane also react with $HgCl_2$ as in the case of biferrocene, giving orange-yellow precipitates with a color that is very similar to that of ferrocene–$7HgCl_2$. The products are less stable than the biferrocene–$2HgCl_2$ adduct; i.e., they change color to blue-green after being allowed to stand at room temperature for several days after preparation. However, they are much more stable than the ferrocene–$7HgCl_2$ adduct which completely changes from orange-yellow to blue-green within a day.

The results indicate that the diferrocenylmethane- and 1,2-diferrocenylethane–$6HgCl_2$ adducts have Fe–Hg bonds, although the bonds seem to be a little weaker than the Fe–Hg bond in the biferrocene–$2HgCl_2$ adduct. Actually, the doublet component with a large Q.S. value decreases and a broad-line component with a small Q.S. value increases in their Mössbauer spectra (Fig. 2), if the compounds are placed in air for several days.

Biferrocene, 1,12-dimethyl[1.1]ferrocenophane and [2.2]-ferrocenophane react with $HgCl_2$ in ethanol giving dark-green paramagnetic precipitates. The ^{57}Fe-Mössbauer spectra of these reaction products are shown in Fig. 3, and the Mössbauer parameters are also listed in Table 1. A smaller Q.S. value (1.87 mm s^{-1} at 78 K) compared with that of biferrocenylene (2.44 mm s^{-1} at 78 K) was found and assigned to an averaged valence state of Fe(II) and Fe(III) as expected from the dark color of the adduct. The Q.S. value is close to that of biferrocenylenium

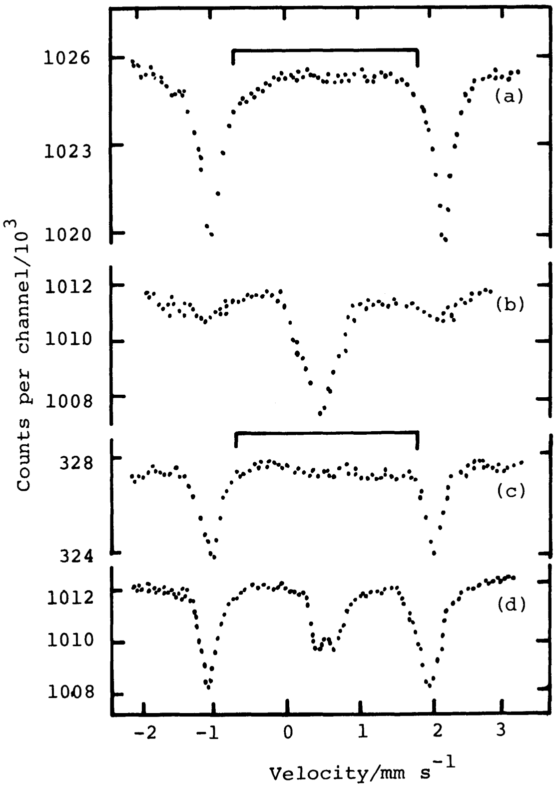


Fig. 2. Mössbauer spectra at 78 K of (a) diferrocenylmethane–$6HgCl_2$ adduct immediately, (b) 7 d after preparation, (c) 1,2-diferrocenylethane–$6HgCl_2$ adduct immediately, (d) 7 d after preparation. Peak position of diferrocenylmethane and 1,2-diferrocenylethane is shown.

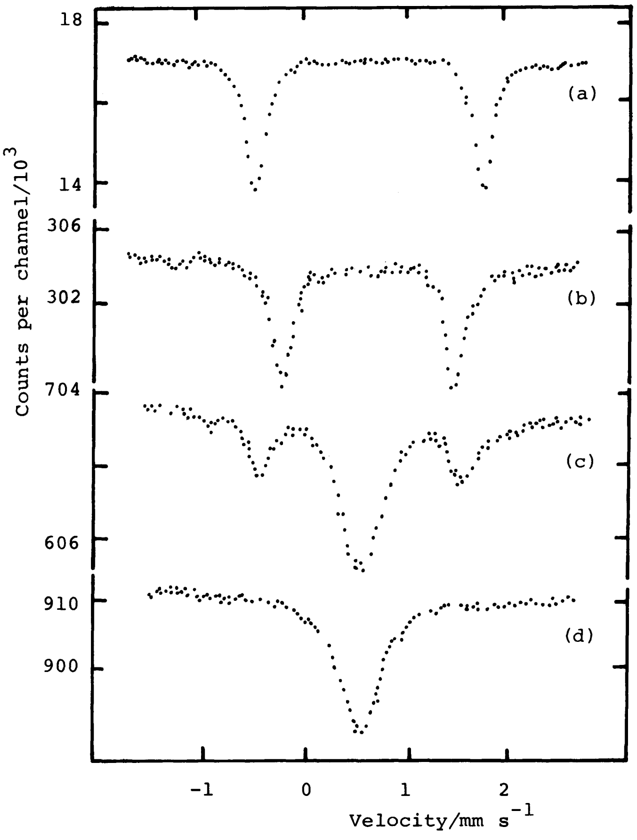


Fig. 3. Mössbauer spectra at 78 K of (a) biferrocenylene, and reaction products of (b) biferrocenylene, (c) 1,12-dimethyl[1.1]ferrocenophane, (d) [2.2]ferrocenophane with $HgCl_2$.

pentaiodide (1.756 mm s^{-1} at 4.2 K), which is known to show a typical averaged valence state.[10]

Magnetic susceptibility measurements showed that the monocationic biferrocenylenium salt is paramagnetic. The effective magnetic moment in a temperature range from 78 K to 120 K was found to be 2.02 BM, also close to the value characteristic of binuclear ferrocene derivatives in an averaged valence state (e.g., 1.90 BM for biferrocenylenium pentaiodide).[10] The results indicate that biferrocenylene is partially oxidized by $HgCl_2$ to form an averaged valence state of a monocationic biferrocenylenium salt.

The 1,12-dimethyl[1.1]ferrocenophane–$HgCl_2$ product showed two quadrupole splitting doublets (Q.S.; 1.93 mm s^{-1}. I.S.; 0.52 mm s^{-1} and Q.S.; 0.0 mm s^{-1}, I.S.; 0.53 mm s^{-1} at 78 K). These values are almost the same as those for the monocationic 1,12-dimethyl[1.1]ferrocenophanium triiodide salt.[10] This fact suggests that an interaction takes place between the iron atom, however, the interaction is not as strong as that of biferrocenylenium.

[2.2]Ferrocenophane reacts with $HgCl_2$ in ethanol giving dark green precipitates which are expressed as [2.2]ferrocenophanium^{2+}($HgCl_3^-$)$_2$. In the Mössbauer spectra of this compound, only a broad singlet peak is observed, suggesting that [2.2]ferrocenophane is oxidized by $HgCl_2$ completely to a dicationic [2.2]ferrocenophanium species.

In the cyclic voltammograms of biferrocenylene and 1,12-dimethyl[1.1]ferrocenophane, two kinds of one-electron oxidation peaks (0.26_5 and 0.85_5 V for biferrocenylene,[22] 0.38 and 0.61 V for 1,12-dimethyl-[1.1]ferrocenophane) were observed, while only one two-electron oxidation peak (0.42 V) was found in that of [2.2]ferrocenophane. The difference between the first and second half-wave potentials, $\Delta E_{1/2}$, has often been used as a parameter of the interaction between the Fe–Fe atoms in binuclear ferrocene derivatives. The fact that a larger value of $\Delta E_{1/2}$ (0.59 V) is observed in the biferrocenylene than the value (0.23 V) found in 1,12-dimethyl[1.1]ferrocenophane, is in accordance with the results of Mössbauer spectroscopic studies on binuclear ferrocenophanes' monocationic salts.

It can be concluded that doubly-bridged ferrocenophanes react with $HgCl_2$ gving only a ferricinium salt and not an adduct containing an Fe–Hg chemical bond. The reason that biferrocene, diferrocenylmethane, and 1,2-diferrocenylethane form adducts with $HgCl_2$ can be explained by assuming a more flexible molecular structure compared with the rigid structure of biferrocenylene, 1,12-dimethyl[1.1]ferrocenophane and [2.2]ferrocenophane. A large conformational change in such a way that the two Fe atoms are ligated to the $HgCl_2$ may occur, for instance, in biferrocene–2$HgCl_2$ but such a change can not be allowed in a rigid structure of binuclear ferrocenophanes.

Based on this speculation, more stable $HgCl_2$ adducts were prepared using ferrocenylruthenocene derivatives. The results of the cyclic voltammography of ferrocenylruthenocene show two one-electron oxidation peaks (E_{ox}; 0.45 and 0.92 V), one is ascribed to an oxidation of ferrocene-type iron atoms (0.45 V) and the other is to that of a ruthenocene-type ruthenium atoms (0.92 V); i.e., Ru atoms are oxidized less easily than Fe atoms by $HgCl_2$ in this compound. It is known that ruthenocene itself reacts with various kinds of Lewis acids such as I_2, $SnCl_4$, $SbCl_5$, and $HgCl_2$, to give relatively stable products containing a chemical bond between Ru and the Lewis acids.[1–4]

Ferrocenylruthenocene reacts with a large excess of $HgCl_2$ in diethyl ether giving diamagnetic orange-yellow precipitates. The product, expressed ferrocenylruthenocene–5$HgCl_2$, is more stable in air than biferrocene–2$HgCl_2$. The biferrocene–2$HgCl_2$ adduct changes color to green–blue upon standing at 80 °C for 2hr, while the color of ferrocenylruthenocene–5$HgCl_2$ remains upon standing under the same conditions.

Typical Mössbauer spectra of ferrocenylruthenocene and its $HgCl_2$ adduct are shown in Fig. 4. The Q.S. value of ferrocenylruthenocene is 2.36 mm s^{-1} at 78 K as shown in Table 1, which is nearly the same as that of biferrocene (2.33 mm s^{-1} at 78 K), suggesting there is no direct effect of ruthenocenyl group on Fe atoms in ferrocenylruthenocene.

A larger Q.S. value is observed in ferrocenylruthenocene–5$HgCl_2$ adduct (2.99 mm s^{-1} at 78 K) compared with the value of the original ferrocenylruthenocene.

Ferrocenylruthenocenylmethane reacts with $HgCl_2$

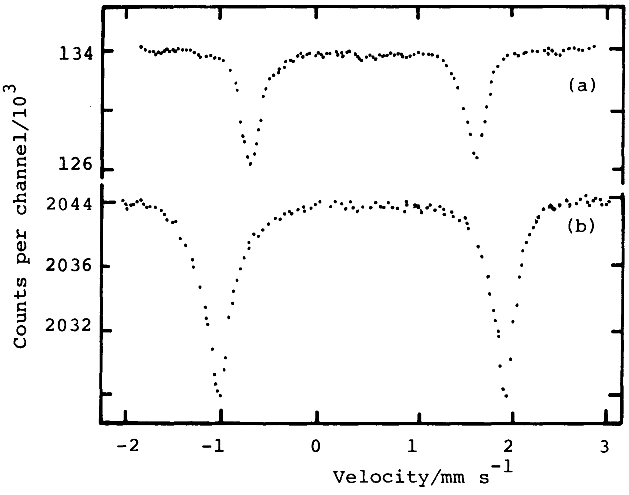
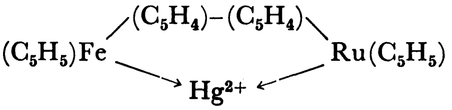


Fig. 4. Mössbauer spectra of (a) ferrocenylruthenocene and (b) its $HgCl_2$ adduct, both at 78 K.

in diethyl ether, giving a diamagnetic orange-yellow product. The Q.S. value found in this adduct (2.84 mm s^{-1} at 78 K) is a little smaller than those of binuclear ferrocene derivatives-$HgCl_2$ adducts or ferrocenylruthenocene-$5HgCl_2$ adduct, but still larger than that of the original ferrocenylruthenocenylmethane (2.44 mm s^{-1} at 78 K). The results indicate that the ferrocenylruthenocenylmethane adduct has an Fe-Hg bonding, although the bond should be a little weaker than the Fe-Hg bond in the $HgCl_2$ adduct of ferrocenylruthenocene.

Actually, the $HgCl_2$ adduct of ferrocenylruthenocenylmethane is not as stable as the $HgCl_2$ adduct of ferrocenylruthenocene. After being allowed to stand in air for several days after preparation, the color of the adduct gradually changed into blue-green, as in the case of diferrocenylmethane-$6HgCl_2$ and 1,2-diferrocenylethane-$6HgCl_2$ adducts. The reason that ferrocenylruthenocenylmethane forms a less stable adduct can be explained by the larger distance between the Ru and Fe atoms in the molecule compared in the ferrocenylruthenocene molecule; i.e., the distance of Fe-Ru atoms may be too large to make a stable chelation like ferrocenylruthenocene-$5HgCl_2$ adduct.

The facts that ferrocenylruthenocene can provide a more stable adduct than biferrocene and ferrocenylruthenocenylmethane with $HgCl_2$ and that the Q.S. value is similar to that of biferrocene-$2HgCl_2$ adduct, also suggest a possibility of chelation,


$(C_5H_5)Fe\begin{array}{c}\diagup(C_5H_4)-(C_5H_4)\diagdown \\ \searrow Hg^{2+} \swarrow\end{array}Ru(C_5H_5)$ rather than a monodentated donation such as $-(C_5H_5)Ru{\rightarrow}Hg^{2+}{\leftarrow}Fe(C_5H_5)(C_{10}H_8)(C_5H_5)Ru{\rightarrow}Hg^{2+}{\leftarrow}Fe(C_5H_5)-$. It is tentatively concluded in this study that ferrocenylruthenocene and biferrocene form very stable adducts with $HgCl_2$ because of an appropriate distance between the Fe-Ru or Fe-Fe atoms for chelation to take place in these adducts. However, further studies must be conducted to provide direct evidece to prove the chelating bond in the adducts.

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