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MÖSSBAUER SPECTROSCOPIC STUDIES OF MERCURY(II) CHLORIDE ADDUCTS OF BIFERROCENE AND BIFERROCENYLENE

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Biferrocene and biferrocenylene react with $HgCl_2$ in diethyl ether to give their $HgCl_2$ adducts. In the ^{57}Fe-Mössbauer spectrum, the former shows a large quadrupole splitting value, suggesting the presence of a direct interaction between the Fe and Hg atoms and the latter shows a smaller quadrupole splitting value, indicating the presence of the averaged-valence state of Fe(II) and Fe(III).

Since the preparation of biferrocene[1)] and biferrocenylene,[2,3)] which are binuclear ferrocene derivatives, their structures and electronic states have been investigated by means of various kinds of physicochemical techniques,[4,5)] and ^{57}Fe-Mössbauer spectroscopic technique has been applied to the investigation,[6-9)] since the quadrupole splitting (Q. S.) value well reflects the chemical state - especially the configuration of d-electrons - around iron atoms, although the isomer shift (I. S.) value is not as sensitive as Q. S. to the electronic state in these compounds. These compounds were oxidized by iodine to give dark colored precipitates, biferrocenium triiodide and biferrocenylenium pentaiodide, respectively.[3,4,8,9)] Based on the ^{57}Fe-Mössbauer spectroscopic studies of these salts, it was found that the former gives two different valence states of iron, corresponding to ferrocene-like Fe(II) and ferricinium-like Fe(III) states, while the latter gives a kind of iron atom in an equivalent valence state which averages these two different states.

Recently, we reported the ^{57}Fe-Mössbauer spectroscopic studies of the HgX_2 adduct of [2]ferrocenophanes syntesized with HgX_2 and [2]ferrocenophanes in diethyl ether,[10)] where X stands for Cl, I, ClO_4, and BF_4. The Q. S. value of the adducts (e. g., 3.27 mm s^{-1} for $[(C_5H_4CH_2)_2Fe]\cdot 3HgCl_2$ at 78 K) is one of the largest among the reported values for most ferrocene derivatives, suggesting an Fe-Hg bonding interaction. The [2]ferrocenophane-$HgCl_2$ adduct is found to be very stable; i. e., the orange-red color of the adduct remains on standing at room temperature more than four months, while ferrocene gives only an unstable adduct with $HgCl_2$ which immediately changes into a dark blue colored ferricinium salt.[11)] In addition to the mercury(II) salt adducts, [2]ferrocenophane-tin(IV) chloride adduct was also reported,[12)] but the studies have so far been limited only to the use of [2]ferrocenophanes, because the tilted cyclopentadienyl ring structure was considered to be in favor of donation of the non-bonding electrons of iron atoms. The present work was planned to study the possibility of producing an adduct of biferrocene or biferrocenylene with $HgCl_2$, which could be expected to give more stable adducts than ferrocene itself, because of the possibility of chelation of the Fe atoms in the binuclear ferrocene derivatives with an 'acid' such as mercury ions.

Biferrocene was prepared by the method previously reported,$^{1)}$ and its $HgCl_2$ adduct was prepared from the following reaction. Biferrocene of 100 mg was dissolved into 50 ml of diethyl ether. To this solution a large excess of $HgCl_2$ (500 mg) dissolved in diethyl ether was added, and the dark-red precipitates formed were filtered, washed with diethyl ether and dried in a vacuum. Found; C, 25.71; H, 2.71%. Calcd for biferrocene·$2HgCl_2$: C, 26.29; H, 1.97%.

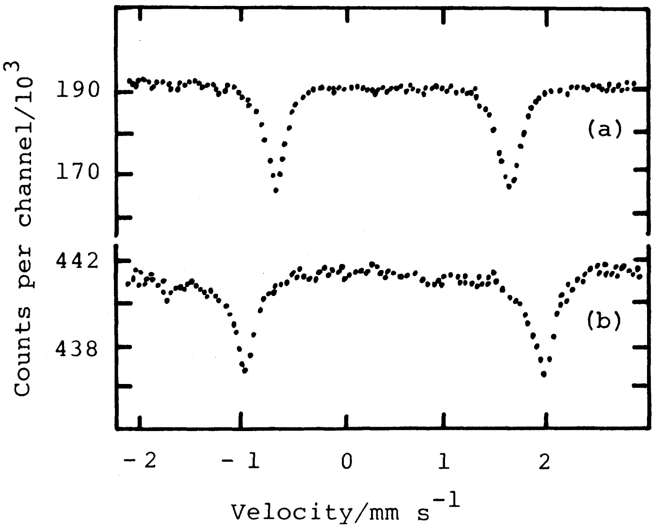

Fig. 1. Mössbauer spectra of (a) biferrocene and (b) biferrocene-$HgCl_2$ adduct, both at 78 K.

Biferrocenylene was prepared by the previous method,$^{2)}$ and its $HgCl_2$ adduct was prepared in ethanol by following the method similar to that used for the biferrocene-$HgCl_2$ adduct. The dark-green precipitates formed were filtered, washed with diethyl ether and dried in a vacuum. Found; C, 16.86; H, 1.13; Hg, 54.00%. Calcd for biferrocenylenium$^+$$(HgCl_3)^-$·$3HgCl_2$: C, 16.11; H, 1.07; Hg, 53.86%.

^{57}Fe-Mössbauer spectroscopic measurements were carried out by using a ^{57}Co(Pt) source moving in a constant acceleration mode. The I. S. values were determined related to metallic iron foil. The experimental errors of the I. S. and Q. S. values are 0.02 mm s^{-1}.

It has been reported that ferrocene reacts with $HgCl_2$ in diethyl ether giving only unstable red-orange precipitates; i. e., on standing at room temperature, it changes the color into blue indicating the formation of a ferricinium salt.$^{11)}$

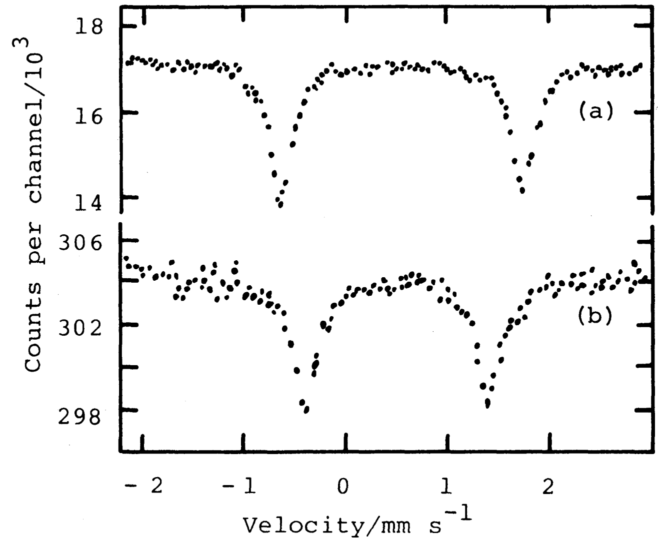

Fig. 2. Mössbauer spectra of (a) biferrocenylene and (b) biferrocenylenium-$HgCl_2$ adduct, both at 78 K.

On the contrary, biferrocene reacts with $HgCl_2$ in the same condition giving stable dark-red precipitates. Figure 1 shows ^{57}Fe-Mössbauer spectra of biferrocene adduct with $HgCl_2$, which is tentatively expressed to be $[(C_5H_4)(C_5H_5)Fe]_2 \cdot 2HgCl_2$ based on the elemental analysis, although further refinement is needed because of the not negligible inconsistencies in the data of elemental analysis. As is seen in Table 1, an anomalously large Q. S. value (2.93 mm s^{-1} at 78 K) is found compared with the value of biferrocene (2.33 mm s^{-1} at 78 K) and is almost the same as that of the unstable ferrocene-$HgCl_2$ adduct (3.09 mm s^{-1} at 78 K), indicating that the electric field gradient around the Fe nucleus in the $HgCl_2$ adduct is distorted largely from that of ferrocene moieties, that is, indicating the presence of a direct interaction between Fe-Hg atoms in the adduct.

On the other hand, biferrocenylene reacts with $HgCl_2$ in ethanol giving dark-green precipitates, the color of which is rather similar to that of ferricinium salts. From the ^{57}Fe-Mössbauer spectrum of biferrocenylene-$HgCl_2$ adduct shown in Fig. 2, a smaller Q. S. value (1.87 mm s^{-1} at 78 K) is found compared to the value of biferrocenylene (2.44 mm s^{-1} at 78 K). The value can be assigned to an averaged valence state of Fe(II) and Fe(III), as expected from the dark-green color of the adduct and in the comparison with the Q. S. value of biferrocenylenium pentaiodide. In other words, biferrocenylene was partially oxidized by the $HgCl_2$ to form an averaged valence state of monocationic biferrocenylenium salt, although the detailed chemical state of counteranions remains undetermined because of slight inconsistencies in the results of elemental analysis.

The magnetic susceptibility measurement shows that the monocationic biferrocenylenium salt is paramagnetic and that the effective magnetic moment in 78-120 K is 2.02 BM which is close to the value characteristic of binuclear ferrocene derivatives in an averaged valence state (e. g., 1.99 BM for biferrocenium pentaiodide).

Table 1. Mössbauer parameters of ferrocene derivatives, their salts, and adducts

Compound	Temp /K	Q. S./mm s^{-1}	I. S./mm s^{-1}
Biferrocene	78	2.33	0.53
Biferrocene$\cdot 2HgCl_2$	78	2.93	0.55
Biferrocenylene	78	2.44	0.54
	300	2.40	0.41
Biferrocenylenium$^+(HgCl_2)^- \cdot 3HgCl_2$	78	1.87	0.53
Biferrocenylenium$^+I_5^-$ a)	4.2	1.756	0.542
	300	1.719	0.441
Ferrocene	78	2.41	0.52
Ferrocene$\cdot 7HgCl_2$ b)	80	3.09	0.53
	275	2.94	0.45

a) Data were taken from Ref. 8.

b) An unstable adduct. Data were taken for the fresh sample reported in Ref. 11.

In order to discuss the results of Mössbauer spectroscopic studies, it is desirable to know about the values of the half-wave redox potentials for biferrocene and biferrocenylene compounds. On the results of the cyclic voltammogram of the biferrocene in CH_2Cl_2, two one-electron oxidation peaks ($E_{1/2}$ = 0.435 and 0.785 V) were reported, while largely separated two one-electron peaks ($E_{1/2}$ = 0.265 and 0.855 V) were reported for the biferrocenylene by C. Levanda et al.[13] Therefore, biferrocenylene compound is supposed to be oxidized by $HgCl_2$ more easily, than biferrocene is, because it can have an averaged valence state.

On the basis of the results presented above, it is concluded that biferrocene reacts with $HgCl_2$ giving a stable $HgCl_2$ adduct, including the Fe-Hg bonding interaction; while biferrocenylene reacts with $HgCl_2$ giving monocationic species of biferrocenylenium, in which there is only one valence state of iron atoms on the Mössbauer time scale, without forming a strong Fe-Hg bonding interaction.

The reason why the biferrocene forms a stable adduct with $HgCl_2$ is explained by assuming its more flexible molecular structure compared with the rigid structure of biferrocenylene which has doubly bridged ferrocene moieties. The slightly smaller value of Q. S. in biferrocene-$HgCl_2$ adduct compared to those in the unstable ferrocene-$HgCl_2$ adduct and in the [2]ferrocenophane-$HgCl_2$ adduct suggests that the biferrocene should react with a mercury(II) ion as a chelating agent, although further structural investigations are needed to confirm the conclusions.

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