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Mössbauer Studies of Mercury(II) Salt Adducts of [2]Ferrocenophane Derivatives

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Various adducts of mercuric salts with [2]ferrocenophane and 1,1,2,2-tetramethyl[2]ferrocenophane, were prepared by treating HgX_2 ($X=Cl^-$, I^-, CN^-) with the [2]ferrocenophane derivatives in ether. The adducts were studied by Mössbauer spectroscopy and other physicochemical measurements. Anomalously large quadrupole splitting values of the adducts (about 3.10—3.30 mm s^{-1} at 78 K) suggest the presence of a strong direct interaction between the Fe and Hg atoms.

Since the discovery of ferrocene, the bonding states of this compound and its oxidized compounds, ferrocenium salts, have been investigated by various physicochemical measurements. Mössbauer spectroscopy has been applied to the investigation as one of the most useful tools to study the chemical state of iron atoms and it was found that Mössbauer parameters of ferrocene and ferrocenium salts are 2.41 mm s^{-1} and ≤ 0.5 mm s^{-1} in quadrupole splitting (Q.S.) value and 0.52 mm s^{-1} in isomer shift (I.S.) value both at 78 K. For most of the ferrocene and ferrocenium derivatives, the variation in isomer shift is slight, while the quadrupole splitting ranges from about 2.5 to 2.0 mm s^{-1} and 0 to 0.5 mm s^{-1}, respectively, depending upon the chemical state, such as the kind of substituent attached to the cyclopentadienyl rings.

Roger M. G. Roberts *et al.* recently reported Mössbauer spectroscopic studies of the $HgCl_2$ adduct of ferrocene synthesized from $HgCl_2$ and ferrocene in ether.[1] The Q.S. values of the adduct (3.09 mm s^{-1} at 78 K and 2.94 mm s^{-1} at 298 K) are one of the largest among values reported for most ferrocene derivatives suggesting an iron–mercury bonding interaction, although the adduct is not stable; *i.e.*, the orange-red color of the adduct changes into blue on standing at room temperature. Magnetic susceptibility measurements at room temperature have shown that the orange-red $Fe(Cp)_2\cdot 7HgCl_2$ compound is diamagnetic and the blue $Fe(Cp)_2\cdot 7HgCl_2$ compound paramagnetic with a magnetic moment of 2.36 BM, ($1\ BM=9.274078\times 10^{-24}\ J\ T^{-1}$). This corresponds to that of a ferrocenium salt.[2]

Based on these results, it was concluded that there should be some kind of bonding interaction between Fe and Hg atoms in the orange compound, while on standing at room temperature the compound would suffer from a slow oxidation accompanying the Fe–Hg bond rupture.

Another interesting observation on the large quadrupole splitting value (2.72 mm s^{-1} at 80 K) was reported by R. M. G. Roberts *et al.* for the $Fe(Cp)_2$–$HAlCl_4$ adduct, suggesting an interaction between iron and hydrogen atoms.[3]

On the other hand, [2]ferrocenophane, one of the bridged ferrocenophane derivatives, was synthesized by H. L. Lentzner and W. E. Watts in 1971.[4] The structure was investigated by X-ray structural analysis and it was found that the cyclopentadienyl rings are inclined at *ca.* 23° to each other.[5] Various other studies of NMR,[4] electronic spectroscopy[4] and electric dipole moment measurements[6] on the [2]ferrocenophane are consistent with the "naked" structure of the iron atom in this compound. The present work was planned to study the possibility of producing an adduct of [2]ferrocenophane–HgX_2 ($X^-=Cl^-$, ClO_4^-, BF_4^-), which can be expected to be more stable than the ferrocene–$HgCl_2$ adduct because of the "naked" structure of iron atoms in the tilted-ring molecular structure.

Experimental

Materials. [2]Ferrocenophane$\cdot 3HgCl_2$ was prepared by mixing [2]ferrocenophane (1.0 g) dissolved in 50 ml diethyl ether with a large excess of $HgCl_2$ dissolved in diethyl ether. The red-orange precipitates were filtered, washed with ether and dried under vacuum. Calcd for $C_{12}H_{12}Fe\cdot 3HgCl_2$: C, 14.03, H, 1.16. Found: C, 13.18; H, 1.21.

1,1,2,2-Tetramethyl[2]ferrocenophane$\cdot 3HgCl_2$ was synthesized by the same method as that used for [2]ferrocenophane$\cdot 3HgCl_2$. Calcd for $C_{16}H_{20}Fe\cdot 3HgCl_2$: C, 17.97; H, 2.18%. Found: C, 18.00; H, 2.00%.

[2]Ferrocenophane$\cdot 0.5Hg(ClO_4)_2$ was prepared by mixing [2]ferrocenophane (0.21 g) dissolved in 150 ml absolute ethanol with about 10 drops of perchloric acid. Yellow-orange crystals started to precipitate. The precipitates were filtered, washed with absolute ethanol and dried under vacuum. Calcd for $C_{12}H_{12}Fe\cdot 0.5Hg(ClO_4)_2$: C, 34.97; H, 2.91%. Found: C, 32.88; H, 2.90%.

[2]Ferrocenophane$\cdot 0.5Hg(BF_4)_2$ was prepared by mixing [2]ferrocenophane (113 mg) with $Hg(CN)_2$ (0.32 mmol) each in 100 ml of absolute ethanol. To the solution, approximately 8 drops of 50% aqueous tetrafluoroboric acid was added. Yellow-orange crystals started to precipitate and the precipitates were filtered, washed with absolute ethanol and dried under vacuum. Calcd for $C_{12}H_{12}Fe\cdot 0.5Hg(BF_4)_2$: C, 36.08; H, 3.00%. Found: C, 35.92; H, 2.91%.

Measurements. ^{57}Fe-Mössbauer measurements were carried out using a ^{57}Co(Pt) source moving in a constant acceleration mode. The isomer shifts were determined relative to metallic iron foil. The experimental errors of the isomer shift and quadrupole splitting values are 0.02 mm s^{-1}. Electronic absorption spectra were measured in an acetonitrile solution with a Hitachi spectrophotometer model-220.

Results and Discussion

It has been reported that ferrocene reacts with $HgCl_2$ in ethanol or ether giving red-orange precipi-

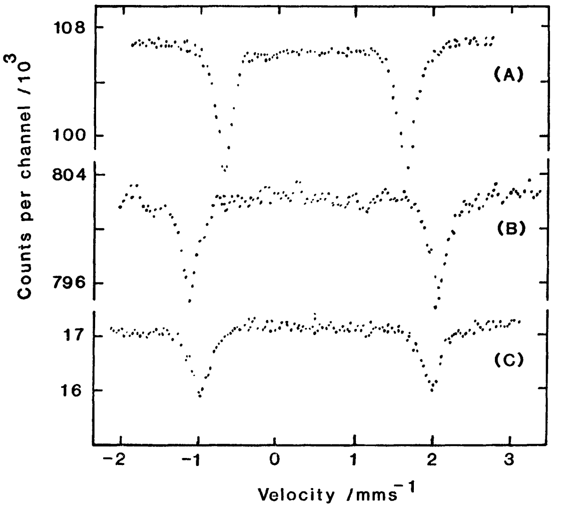

Fig. 1. Mössbauer spectra of (A) [2]ferrocenophane, (B) [2]ferrocenophane-$3HgCl_2$ adduct, and (C) [2]-ferrocenophane-$0.5Hg(BF_4)_2$ adduct all at 78 K.

tates. On standing at room temperature, this complex is also known to change color to blue. On the other hand, the present studies revealed that [2]ferrocenophane reacts with $HgCl_2$ in ether or ethanol giving red-orange precipitates, which are stable on standing, without change of color. Mössbauer spectra of [2]ferrocenophane and its mercury(II) chloride adduct are shown in Fig. 1. The quadrupole splitting of [2]ferrocenophane is found to be 2.41 mm s^{-1}, and that of 1,1,2,2-tetramethyl[2]ferrocenophane, 2.36 mm s^{-1}, both at 78 K. These values are almost the same as that of ferrocene (2.41 mm s^{-1}), indicating that the electric field gradient at the Fe nucleus in [2]ferrocenophane remains almost the same as that of ferrocene, although the cyclopentadienyl rings are largely inclined by *ca.* 23° each other.

A similar observation was reported by R. A. Abramovitch *et al.* in 1975 for 1-thia-2-aza[2]ferrocenophane 1,1-dioxide, in which cyclopentadienyl rings were bridged by sulfur and nitrogen atoms instead of carbon atoms.[7] The quadrupole splitting value of this compound is almost the same as that of ferrocene, as in the case of [2]ferrocenophane.

On the contrary, a remarkable difference was observed in the Mössbauer spectra of mercury(II) halide adducts of [2]ferrocenophane derivatives from that of ferrocene. The quadrupole splitting value of [2]ferrocenophane·$3HgCl_2$ is 3.29 mm s^{-1} at 78 K, which is the largest of all the reported ferrocene derivatives, while the Q.S. value of ferrocene·$7HgCl_2$ has been reported to be 3.09 mm s^{-1} at 78 K.

The large Q.S. value of [2]ferrocenophane·$3HgCl_2$ compound compared with that of ferrocene·$7HgCl_2$ suggests a stronger bonding formed between iron and mercury atoms in the adduct. The suggestion may also be supported by the fact that the [2]ferrocenophane·$3HgCl_2$ adduct remains more stable on standing, even after 180 d, than the ferrocene·$7HgCl_2$ adduct which changes to the ferrocenium salt. The results imply that the bonding formed by the "naked" electrons of Fe atom coordinating with an orbital of a Hg atom is so stable that the red-orange color of the mercury(II) chloride adduct of [2]ferrocenophane does not change on standing. The quadrupole splitting value of the mercury(II) iodide adduct, 1,1,2,2-tetramethyl[2]ferrocenophane·$2HgI_2$, is a little smaller than that of the mercury(II) chloride adduct of [2]-ferrocenophane.

D. N. Hendrickson *et al.* reported the structure and bonding state of ruthenocene compounds such as $[(Cp)_2Ru]_2HgX_2$ ($X=PF_6^-$, BF_4^-, ClO_4^-) by means of various physicochemical techniques.[8] It was found that a strong line component remained unchanged in the Raman spectra of $[(Cp)_2Ru]_2HgX_2$ except for the absorptions attributable to the different kinds of anion and that the strong Raman band observed at 110 cm^{-1} both in solid and in a solution containing the cation was assigned to a symmetrical Ru–Hg–Ru stretching mode. In their study of the electronic absorption spectrum of $[(Cp)_2Ru]_2Hg(PF_6)_2$ at room temperature, a strong new absorption band was observed at 320 nm and assigned to a transition associated with the Ru–Hg–Ru unit, based on studies of $M_2(CO)_{10}$ (M=Mn, Re) complexes.[9] From their results, they proposed that the structure of $[Ru(Cp)_2]_2HgX_2$ should be expressed as $[(Cp)_2Ru(II)–Hg(II)–Ru(II)(Cp)_2]X_2$.

Although ferrocene does not react with mercury(II) cyanide and does not form $[(Cp)_2Fe–Hg–Fe(Cp)_2]^{2+}$ but produces the ferrocenium salt, [2]ferrocenophane derivatives react with mercury(II) cyanide and produce mercury(II) salt adducts, $[(C_5H_4CH_2)_2Fe]_2HgX_2$, ($X^-=ClO_4^-, BF_4^-$), under similar conditions. Mössbauer parameters of the compounds are listed in Table 1 and typical Mössbauer spectra of the mercury(II) salt adducts are also shown in Fig. 1. The quadrupole splitting values of [2]ferrocenophane·$0.5Hg(BF_4)_2$ are 3.11 mm s^{-1} at 78 K and 3.10 mm s^{-1} at 300 K, and those of 1,1,2,2-tetramethylferrocenophane·$0.5Hg(BF_4)_2$ are 3.12 mm s^{-1} at 78 K and 3.08 mm s^{-1} at 300 K. Both values are larger than those of [2]ferrocenophane and 1,1,2,2-tetramethyl[2]ferrocenophane and are similar to that of mercury(II) chloride adducts, [2]ferrocenophane·$3HgCl_2$. This fact shows

TABLE 1. MÖSSBAUER PARAMETERS OF [2]FERROCENOPHANE, $(C_5H_4CH_2)_2Fe$, AND TETRAMETHYL[2]FERROCENOPHANE, $(C_5H_4C(CH_3)_2)_2Fe$, AND THEIR ADDUCTS WITH MERCURY(II) SALTS

Compound	Temp K	Q.S. mm s^{-1}	I.S. mm s^{-1}
$(C_5H_4CH_2)_2Fe$	78	2.41	0.49
$[(C_5H_4CH_2)_2Fe]·(HgCl_2)_3$	78	3.29	0.49
$[(C_5H_4CH_2)_2Fe]·$ 1/2 $Hg(ClO_4)_2$	78	3.14	0.53
$[(C_5H_4CH_2)_2Fe]·$ 1/2 $Hg(BF_4)_2$	78	3.11	0.53
	300	3.10	0.46
$(C_5H_4C(CH_3)_2)_2Fe$	78	2.36	0.53
$[(C_5H_4C(CH_3)_2)_2Fe]·$ 1/2 $Hg(BF_4)_2$	78	3.12	0.53
	300	3.08	0.44
$[(C_5H_4C(CH_3)_2)_2Fe]·(HgI_2)_2$	78	3.09	0.51

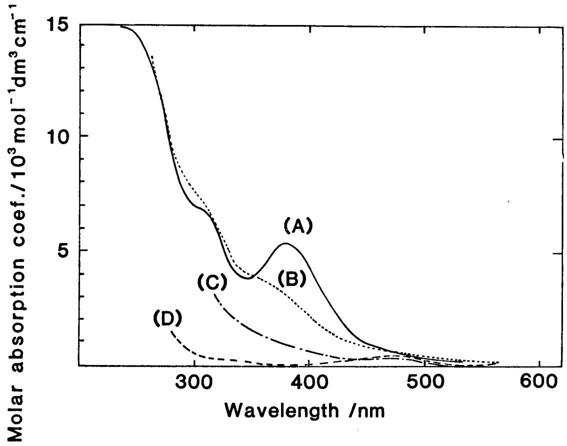

Fig. 2. Absorption spectra of an acetonitrile solution of bis([2]ferrocenophane)mercury(II) perchlorate, $[(C_5H_4CH_2)_2Fe]_2$-$Hg(ClO_4)_2$ (A) 4 min, (B) 20 min, (C) 50 min after preparation, and (D) an acetonitrile solution of [2]ferrocenophane, $(C_5H_4CH_2)_2Fe$.

that there is also a strong interaction between Fe–Hg atoms in these adducts described as $[(C_5H_4CH_2)_2Fe$–Hg–$Fe(C_5H_4CH_2)_2]^{2+}X^-_2$ in a similar way to the structure of $[Ru(Cp)_2]_2HgX_2$.

Figure 2 shows the electronic absorption spectra of $[(C_5H_4CH_2)_2Fe]_2Hg(ClO_4)_2$ dissolved in acetonitrile. A new absorption band, which is similar to that of the $[(Cp)_2Ru]_2HgX_2$ solution in spectral shape, appears at 380 nm, although the intensity of the band decreases gradually as the solution is allowed to stand, probably because of dissociation of the adduct in solution, as found in the solutions of $[(Cp)_2Ru]_2HgX_2$. The results suggest that the absorption band is assigned to an electronic transition associated with the Fe–Hg–Fe unit corresponding to that of the Ru–Hg–Ru unit.

All the results obtained in the present studies lead us to the conclusion that [2]ferrocenophane and 1,1,2,2-tetramethyl[2]ferrocenophane give stable adducts in which a direct bond is formed between iron and mercury atoms and that the bonding is stabilized by coordinating the "naked" electrons of iron atoms to one of the vacant orbitals of mercury atoms in the tilting structure of cyclopentadienyl rings in [2]ferrocenophanes, as in the case of [2]ferrocenophane–tin(IV) chloride adduct.10)

References

1) R. M. G. Roberts, J. Silver, and I. G. Harrison, *J. Organomet. Chem.*, **209**, 385 (1981).

2) W. H. Morrison, Jr., and D. N. Hendrickson, *Inorg. Chem.*, **11**, 2912 (1972).

3) R. M. G. Roberts, J. Silver, R. J. Ranson, and I. E. G. Morrison, *J. Organomet. Chem.*, **219**, 233 (1981).

4) H. L. Lentzner and W. E. Watts, *Tetrahedron*, **27**, 4343 (1971).

5) M. B. Laing and K. N. Trueblood, *Acta Crystallogr.*, **19**, 373 (1965).

6) H. Lumbroso, C. Pigenet, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, **28**, 111 (1972).

7) R. A. Abramovitch, J. L. Atwood, M. L. Good, and B. A. Lampert, *Inorg. Chem.*, **14**, 3085 (1975).

8) D. N. Hendrickson, Y. S. Sohn, W. H. Morrison, Jr., and H. B. Gray, *Inorg. Chem.*, **11**, 808 (1972).

9) R. Levenson and H. B. Gray, unpublished work; R. Leverson, Ph. D. Thesis, Columbia University, New York, N. Y., 1970.

10) M. Watanabe, H. Ichikawa, I. Motoyama, and H. Sano, *Chem. Lett.*, **1983**, 1009.