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^{57}Fe-Moessbauer Spectroscopic Studies on the Products of [1.1]Ferrocenophane-1,12-dione with I_2, Br_2, and DDQ

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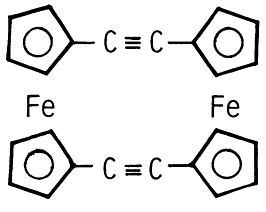
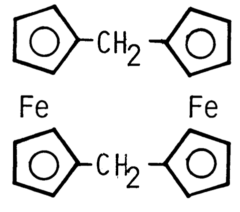
[1.1]Ferrocenophane-1,12-dione reacts with I_2 and DDQ giving a diamagnetic [1.1]ferrocenophane-I_2 and DDQ adduct and reacts with Br_2 giving a paramagnetic [1.1]ferrocenophanium-1,12-dione$^+$ Br_3^- salt. The results of ^{57}Fe-Moessbauer spectroscopy and other physicochemical measurements of the reaction products indicate that the formers are an I_2 and a DDQ molecular complex, while the latter is a trapped-valence type mixed-valence salt.

It has been already known that a number of mixed-valence polynuclear ferrocene compounds can be classified into two types of valence states of Fe atoms, a trapped valence type and an averaged-valence type, by means of ^{57}Fe-Moessbauer spectroscopy. The results of the ^{57}Fe-Moessbauer spectroscopy and other physicochemical measurements of the mixed-valence state of monocationic salts of [2.2]ferrocenophane-1,13-diyne and [1.1]ferrocenophane show that the former's cation is in a valence state averaged over Fe(II) and Fe(III) and the latter's is in a trapped-valence state in the ^{57}Fe-Moessbauer time scale (ca. 10^{-7} s).[1-4] The facts clearly prove that the metal-metal interaction takes place through a conjugate π-system in the mixed valence compounds. [1.1]Ferrocenophane-1,12-dione, first synthesized by W. E. Watts in 1967,[5] has also conjugated π-systems, although the π-electrons might be localized in the CO groups to some extent. On the other hand, it has been discovered for [2]ferrocenophanes and some binuclear biferrocenes that the nonbonding e_{2g} electrons of the Fe atoms in the ferrocenes are ligated to a Lewis acid as in the case of [2]ferrocenophane-2I_2 adduct, giving a larger quadrupole splitting (Q. S.) value than the value of the original ferrocene derivatives.[6-8] In the present report, the results of the ^{57}Fe-Moessbauer spectroscopy and other physicochemical measurements on the reaction products of [1.1]ferrocenophane-1,12-dione with I_2, Br_2, and dichlorodicyanobenzoquinone (DDQ) are described.

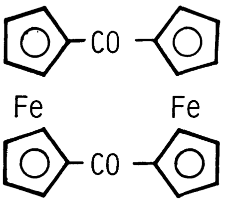
[1.1]Ferrocenophane-1,12-dione was prepared according to the previous report,[5] and its reaction products with I_2, Br_2, and DDQ were prepared from the following reaction. [1.1]Ferrocenophane-1,12-dione (100 mg) was dissolved into 200 cm^3 dry benzene. To this solution a large excess of I_2 (1.0 g) dissolved in dry benzene mixed with hexane was added. The bright yellow precipitates formed were filtered and washed with dry benzene and ether. Found: C, 39.94; H, 2.34%. Calcd for [1.1]ferrocenophane-1,12-dione-I_2, $C_{22}H_{16}O_2Fe_2I_2$: C, 38.98; H, 2.38%. The reaction product of [1.1]ferrocenophane-1,12-dione with Br_2 was prepared by a



[2.2]Ferrocenophane-1,13-diyne



[1.1]Ferrocenophane



[1.1]Ferrocenophane-1,12-dione

method similar to that used for the reaction product with I_2. The yellow-brown precipitates formed were filtered and washed with dry benzene and ether. Found: C, 38.88; H, 2.43%. Calcd for [1.1]ferrocenophane-1,12-dione-1.5Br_2, $C_{22}H_{16}O_2Fe_2Br_3$: C, 39.80; H, 2.43%. [1.1]Ferrocenophane-1,12-dione (100 mg) was dissolved into 100 cm^3 chloroform. To this solution a large excess of DDQ (300 mg) dissolved in benzene mixed with hexane was added. The dark-yellow precipitates formed were filtered and washed with chloroform mixed with hexane. Found: C, 54.87; H, 2.56; N, 4.31%. Calcd for [1.1]ferrocenophane-1,12-dione-DDQ, $C_{30}H_{16}Cl_2O_4N_2Fe_2$: C, 55.34; H, 2.48; N, 4.30%. ^{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 ^{57}Fe was taken 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-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_2Cl_2. ^{13}C-CP-MAS NMR spectra were obtained under the same conditions as in the case of a previous report.$^{9)}$ Chemical shifts were measured with respect to external adamantane and converted to the shifts from TMS.

Typical ^{57}Fe-Moessbauer spectra of the [1.1]ferrocenophane-1,12-dione and its reaction products with the oxidizing reagents are shown in Fig. 1 and the ^{57}Fe-Moessbauer parameters are listed in Table 1. [1.1]Ferrocenophane-1,12-dione shows relatively smaller Q. S. values (2.16 mm s^{-1} at 78 K and 2.17 mm s^{-1} at 300 K) than the value of ferrocene itself (2.41 mm s^{-1} at 78 K) probably because of the electron-attractive carbonyl groups attached to cyclopentadienyl rings. The I_2 product gives a slightly smaller Q. S. doublet (Q. S., 2.05 mm s^{-1} at 78 K and 2.15 mm s^{-1}

Table 1. ^{57}Fe-Moessbauer parameters of [1.1]ferrocenophane-1,12-dione, their adducts, and salt

Compounds	Temp/K	Q. S./mm s^{-1}	I. S./mm s^{-1}
[1.1]Ferrocenophane-1,12-dione	78	2.16	0.52
	300	2.17	0.42
[1.1]Ferrocenophane-1,12-dione-I_2	78	2.05	0.48
	300	2.15	0.44
[1.1]Ferrocenophanium-1,12-dione$^+$ Br_3^-	78	2.12	0.51
		0.35	0.50
[1.1]Ferrocenophane-1,12-dione-DDQ	78	2.18	0.48
	300	2.18	0.44

at 300 K) than the value of the [1.1]ferrocenophane-1,12-dione. The absence of either a broad singlet line or an anomalously larger Q. S. line than that of [1.1]ferrocenophane-1,12-dione indicates that the Fe atom is neither oxidized by I_2 nor bonded with the I atom. The results are in good accordance with the magnetic susceptibility measurements; that is, the reaction product with I_2 is diamagnetic from 78 K to 300 K. Figure 2 shows ^{13}C-CP-MAS NMR spectra of [1.1]ferrocenophane-1,12-dione (a) and its I_2 product (b). The ^{13}C-chemical shift values of the [1.1]ferrocenophane-1,12-dione are found to be 202.3 (CO), 80.0(C_1), 74.4(C_5H_4) and 72.7(C_5H_4) ppm and the values of the I_2 product are found to be 201.2(CO), 79.8(C_1) and 73.1(C_5H_4) ppm. Only small shifts are observed for the reaction product with I_2, although a large low-field shift (20.2 ppm) is found in the reaction of ruthenocene with I_2 giving a ruthenocene-$2I_2$ adduct which contains a Ru-I bond.[9] A TG thermogram of the [1.1]ferrocenophane-1,12-dione shows no weight loss up to 250 °C and that of the crystalline iodine a loss from 60 °C, whereas the reaction product with I_2 shows a weight loss from 110 °C. The facts indicate that the reaction product with I_2 is neither a mixture nor a compound with a metal-I bond but a molecular complex or adduct with a weak interaction between the [1.1]ferrocenophane-1,12-dione and I_2.

A similar observation was also found for the reaction product with DDQ. [1.1]Ferrocenophane-1,12-dione reacts with DDQ giving diamagnetic dark-yellow precipitates which are analyzed as [1.1]ferrocenophane-1,12-dione-DDQ. The Q. S. values of the DDQ product are found to be 2.18 mm s^{-1} at 78 K and 2.19 mm s^{-1} at 300 K, which are in good agreement with the values of [1.1]ferrocenophane-1,12-dione. It can be concluded that the reaction of [1.1]ferrocenophane-1,12-dione with I_2 and DDQ gives their molecular complexes, whereas [2.2]ferrocenophane-1,13-diyne and [1.1]ferrocenophane react with I_2 and DDQ giving monocationic ferrocenium salts.

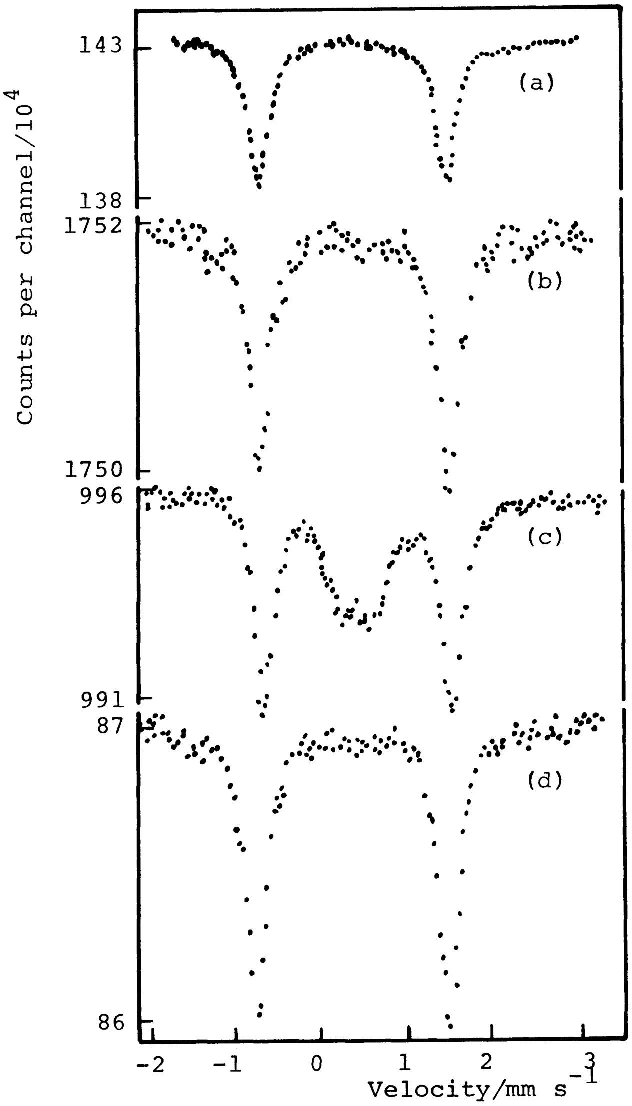


Fig. 1. ^{57}Fe-Moessbauer spectra of [1.1]-ferrocenophane-1,12-dione (a) and its reaction products with I_2 (b), Br_2 (c), and DDQ (d), all at 78 K.

The reason why [1.1]ferrocenophane-1,12-dione cannot be oxidized by I_2 or DDQ can be explained by assuming its high oxidation potential. The results of the cyclic voltammography of [1.1]ferrocenophane-1,12-dione show much higher two one-oxidation potential values ($E_{1/2}$: 0.96 and 1.27 V) than the values of [2.2]ferrocenophane-1,13-diyne and [1.1]-ferrocenophane ($E_{1/2}$: 0.60 and 0.94 V, and 0.48 and 0.70 V in CH_2Cl_2, respectively).

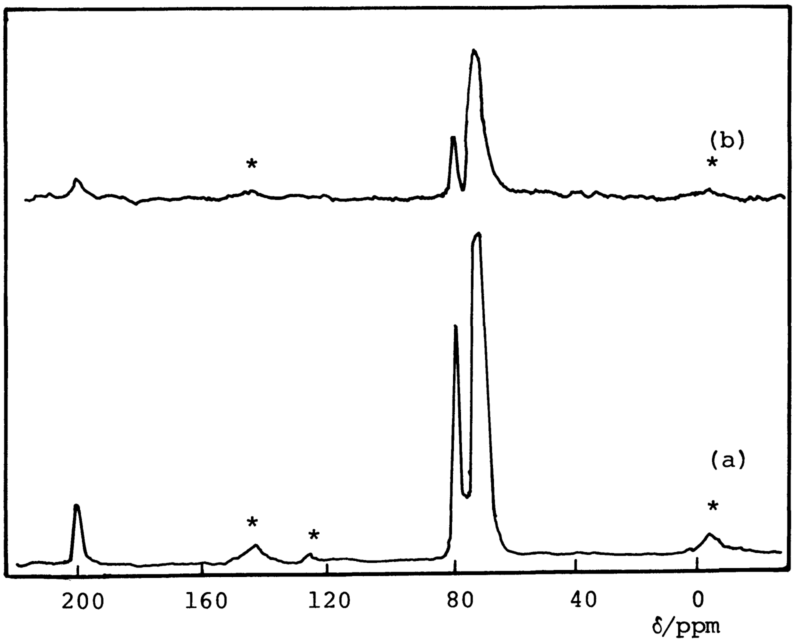


Fig. 2. ^{13}C-CP-MAS NMR spectra of [1.1]ferrocenophane-1,12-dione (a) and its I_2 adduct (b). Star mark (*) indicates spinning side bands.

On the other hand, [1.1]-ferrocenophane-1,12-dione reacts with a large excess of Br_2, giving paramagnetic yellow-brown precipitates. Magnetic susceptibility measurements show that the mean value of effective magnetic moment is estimated to be 2.3 BM in a temperature range from 78 K to 300 K.

The reaction product shows two Q. S. doublets (Q. S., 2.12 and 0.35 mm s^{-1}; I. S. 0.51 and 0.50 mm s^{-1}, respectively, at 78 K) in the ^{57}Fe-Moessbauer spectrum. The results indicate that the electron transfer rate is less than ca 10^7 s^{-1}; that is, there is much weaker interaction between the two Fe atoms, Fe(II) and Fe(III), in the Br_3^- salt than that of monocationic salt of [2.2]ferrocenophane-1,13-diyne.[1)] The conclusion is supported by the electronic absorption spectroscopic study; i.e., little intervalence charge transfer band is observed in the near-infrared region on the spectrum of the mixed valence [1.1]ferrocenophanium-1,12-dione$^+$ Br_3^- salt.

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