CHEMISTRY LETTERS, pp. 1775-1778, 1983. © The Chemical Society of Japan 1983

MÖSSBAUER STUDIES OF BRIDGED FERROCENOPHANE DERIVATIVE'S POLYIODIDES

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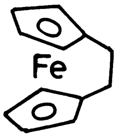
[2]Ferrocenophanes, the ring tilted ferrocene derivatives, were oxidized with iodine in benzene and studied by means of Mössbauer spectroscopy. The quadrupole splitting value of the compounds is found to be 3.70 mm s^{-1} at 78 K, which is one of the largest found in ferrocene derivatives, suggesting the presence of a strong direct interaction between iron atoms and iodine atoms. The results were compared with [3] and [4]ferrocenophane's polyiodides.

It was reported previously that [2]ferrocenophane-metal chloride adducts involve an iron-metal bonding interaction showing one of the largest values in quadrupole splitting, while [3]ferrocenophane-metal chloride adducts consist of a ferrocene-mercury(II) chloride adduct.¹⁾ The results were explained by assuming that the nonbonding electrons (e_{2g} electrons in ferrocene) should be coordinated with vacant orbitals of metal atoms in the case of [2]ferrocenophane adducts, since the tilting Cp ring structure could make the coordination easier. The present studies describe that needle crystals prepared from [2]ferrocenophane by treating with iodine show a quadrupole split line as large as [2]ferrocenophane-metal chloride adducts in the Mössbauer spectrum at liquid nitrogen temperature and a quadrupole split line similar to that found in ferricinium and [3]ferrocenophanium salt at room temperature.



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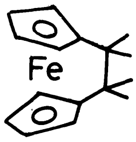

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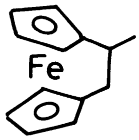

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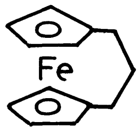

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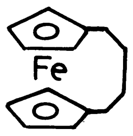

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Compounds **1**, **2**, **4**, and **5** were prepared by the methods reported by Rinehart, Jr. et al.,[2)] Lentzner and Watts,[3)] and Lüttringhaus and Kulick.[4)] Compound **3** was prepared from the reaction of ferrous chloride with dianions of 1,2-dicyclopentadienylpropane, which was obtained by the treatment of 1,2-dibromopropane with sodium cyclopentadienide. The purity of the compound was confirmed by elemental analysis.

Polyiodides of the compounds **1**, **2**, **3**, **4**, and **5** were prepared through the oxidation of the neutral ferrocenophane derivatives with iodine in benzene. Other salts with BF_4^- anions were prepared through the oxidation of the ferrocenophanes in an ether solution of benzoquinone and trifluoroborate, as in the cases of preparation of tetrafluoroborates of most ferricinium derivatives.

^{57}Fe-Mössbauer measurements were carried out by using a ^{57}Co(Pt) source moving in a constant acceleration mode. Isomer shift (I.S.) values were determined relative to metallic iron foil. Experimental errors of the I.S. and quadrupole splitting (Q.S.) value were estimated to be 0.02 mm s^{-1}. Electronic absorption spectra were measured in acetonitrile solutions with a Hitachi spectrometer model EP-3T.

Mössbauer parameters of the compounds used in the present study are listed in Table 1 and Mössbauer spectra of [2], [3], and [4]ferrocenophanium salts are shown in Fig. 1. The Q. S. value of [4]ferrocenophane is found to be 2.31 mm s^{-1}, and that of [3]ferrocenophane 2.29 mm s^{-1}, respectively both at 78 K. Those values are a little smaller than that of ferrocene (2.41 mm s^{-1} at 78 K), but the values of [2]-ferrocenophanes, compounds **1**, **2**, and **3**, are larger than those of [3] and [4]ferrocenophane, as found in Table 1. This discontinuous change may not be accounted for by a simple electric inductive effect of the increased bridged carbon atoms, but be ascribed to an increased asymmetric parameter concerning electric field gradient tensor about iron atom because of the tilting Cp ring structure.

A remarkable difference in the values of Q. S. is found in the products of those compounds with iodine, whereas the salt of BF_4^- with monocations of the compound **2** and triiodide salts of the compound **4** and **5** show an unresolvable singlet peak as in the case of most ferricinium salts. Such larger values of Q.S. cannot be ascribed to an increased asymmetric parameter and are similar to the values (3.14 and 3.49 mm s^{-1} at 78 K) found in mercuric perchlorate adduct, $[(C_5H_4CH_2)_2$-

Table 1. Mössbauer parameters of [2]ferrocenophane (**1**), tetramethyl[2]ferrocenophane (**2**), monomethyl[2]ferrocenophane (**3**), [3]ferrocenophane (**4**), [4]ferrocenophane (**5**), and their salts

	Compound	Temp/K	Q.S./mm s^{-1}	I.S./mm s^{-1}
1	$(C_5H_4CH_2)_2Fe$	78	2.41	0.49
	$[(C_5H_4CH_2)_2FeI]^+I_3^-$	78	3.65 0.86	0.54 0.40
		300	3.65 0.67	0.52 0.40
2	$(C_5H_4C(CH_3)_2)_2Fe$	78	2.36	0.53
	$[(C_5H_4C(CH_3)_2)_2FeI]^+I_3^-$	78	3.70 0.38	0.53 0.20
		200	3.65 0.34	0.54 0.22
		300	3.65 0.50	0.54 0.18
	$[(C_5H_4C(CH_3)_2)_2Fe]^+BF_4^-$	78	<0.5	0.52
		300	<0.5	0.44
3	$(C_5H_4CH(CH_3)CH_2C_5H_4)Fe$	78	2.39	0.53
	$[(C_5H_4CH(CH_3)CH_2C_5H_4)FeI]^+I_3^-$	78	3.66 0.50	0.53 0.39
4	$((C_5H_4CH_2)_2CH_2)Fe$	78	2.29	0.52
	$[((C_5H_4CH_2)_2CH_2)Fe]^+I_3^-$	78	<0.5	0.53
5	$(C_5H_4CH_2CH_2)_2Fe$	78	2.31	0.54
	$[(C_5H_4CH_2CH_2)_2Fe]^+I_3^-$	78	<0.5	0.52

Fe]$_2$·Hg(ClO$_4$)$_2$, and tin chloride [2]ferrocenophane adduct, [((C$_5$H$_4$CH$_2$)Fe)$_2$SnCl$_2$]-(SnCl$_5$)$_2$·2H$_2$O, which are concluded to have a structure similar to ruthenocene mercury(II) or tin(IV) chloride adducts, [(C$_5$H$_5$)$_2$Ru-M^{2+}-Ru(C$_5$H$_5$)$_2$]X$^-_2$, where M^{2+} stand for Hg^{2+} or SnCl$_2$$^{2+}$ and ClO$_4$$^-$ or SnCl$_5$$^-$, respectively.[5]

Based on the analogy to the ruthenocene compounds, it may be reasonable to assume that the iron atoms in [2]ferrocenophanes can coordinate with "acids" such as Hg^{2+}, SnCl$_2$$^{2+}$, and also I$^+$ cations by donating essentially non-bonding electrons (corresponding to e$_{2g}$ electrons in ferrocene) to an unoccupied orbital in the "acid" atoms. Sohn et al. reported that oxidation of ruthenocene by iodine gives [(C$_5$H$_5$)$_2$-RuI]$^+$I$_3$$^-$ and determined the crystal structure by using X-ray analysis, finding that the cyclopentadienyl rings in [(C$_5$H$_5$)$_2$RuI]$^+$ are eclipsed to accomodate I$^+$ cation.[6]

As found in Table 1 and Fig. 2, in addition to the anomalously large Q.S. component, the iodo[2]ferrocenophanium triiodide shows an extra component with a small Q.S. with a little lower I.S. value compared with those of ferricinium-type species in the Mössbauer spectrum at 300 K, although all the mononuclear ferrocene and ferricinium derivatives are known to show only a single spectral component in their spectra. Similar temperature dependence of the decreasing intensity in the larger Q.S. component and the increasing intensity in the smaller Q.S. component is observed with increasing temperature also in the iodine oxidation products of compounds **2** and **3**.

The crystal structure determined by X-ray analysis using a single crystal of the product of tetramethyl[2]ferrocenophane treated with iodine at room temperature indicates that the cyclopentadienyl rings tilt by 41°; i.e., more than in the case of the original [2]ferrocenophane, in which the cyclopentadienyl rings are reported to tilt back by 23°.[7] As seen in Fig. 3, it is found that the iron atoms squeezed

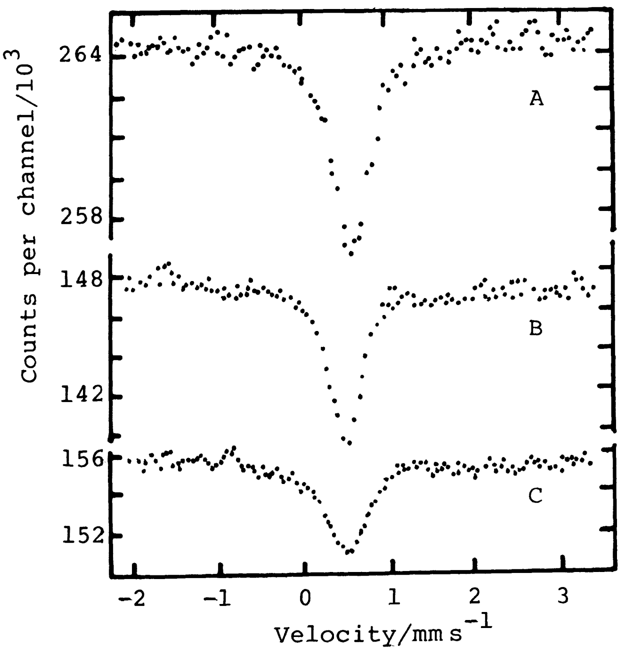

Fig. 1. ^{57}Fe-Mössbauer spectra of]3]ferrocenophanium triiodide (A), [4]ferrocenophanium triiodide (B), and tetramethyl[2]ferrocenophanium tetrafluoroborate (C) at 78 K.

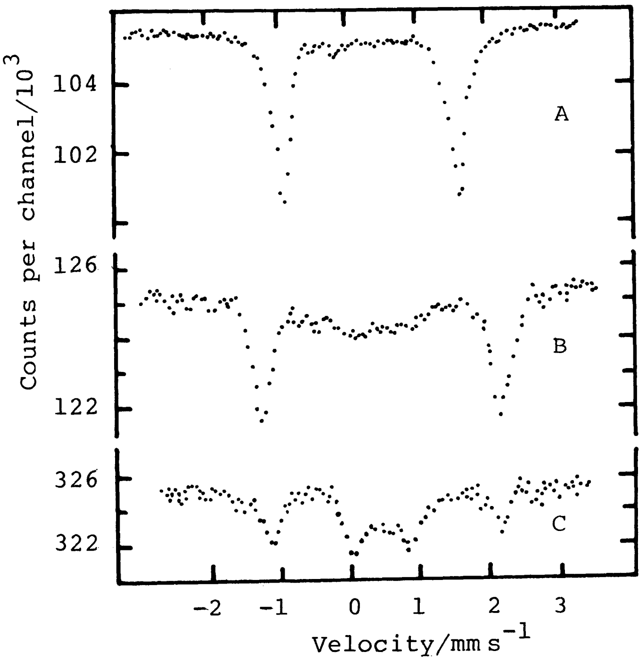

Fig. 2. ^{57}Fe-Mössbauer spectra of [2]ferrocenophane at 78 K (A), iodo-[2]ferrocenophanium triiodide at 78 K (B), and at 300 K (C).

out of the tilted cyclopentadienyl structure have iodine atoms in a short distance. Since there remain disordered and not determined reflections, in addition to triiodide anions, and the Mössbauer spectrum shows the presence of two kinds of species with a large and a small Q.S. value at 300 K, further structural analysis is being carried on at lower temperatures in connection to the Q.S. value of the compound and detailed structural data will be published elsewhere.

Figure 4 compares electronic absorption spectra of some of the acetonitrile solutions of ferricinium, [3]ferrocenophanium, [4]ferrocenophanium, and iodo[2]ferrocenophanium triiodidesand [2]ferrocenophanium tetrafuoloborate. There is no peak component in the range of 600 to 700 nm only for iodo[2]ferrocenophanium triiodide, whereas other compounds show the peak component characteristic of ferricinium-type species at the region.

It may be concluded based on the results that the iodo[2]ferrocenophanium cations have an Fe-I bonding as found in $[(C_5H_5)_2RuI]^+$ cations, and the electronic distribution becomes similar to that coordinated to I^+ cations as in the case of [2]ferrocenophane-metal chloride adducts especially at liquid nitrogen temperature.

The authors are deeply indebted to Prof. Shigeru Minomura and Dr. Michiko Konno for their assistance and discussions on the structural analysis at the Institute for Solid State Physics, The University of Tokyo.

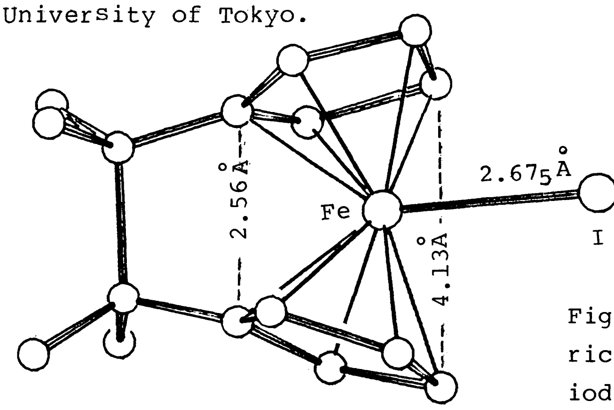

Fig. 3. Profile of an iodotetramethyl[2]ferrocenophanium cation.

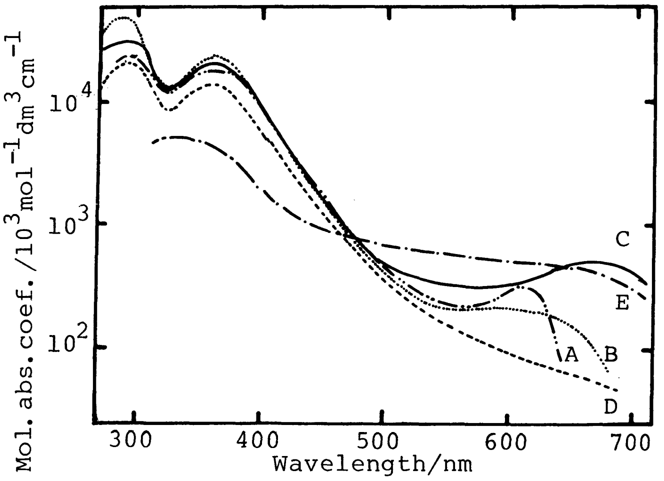

Fig. 4. Electronic absorption spectra of ferricinium triiodide (A), [3]ferrocenophanium triiodide (B), [4]ferrocenophanium triiodide (C), iodo[2]ferrocenophanium triiodide (D), and [2]-ferrocenophanium tetrafluoroborate (E) in CH_3CN.

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(Received August 19, 1983)