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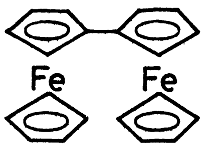
MÖSSBAUER SPECTROSCOPIC STUDY ON THE MIXED- AND AVERAGED-VALENCE FERROCENE DERIVATIVES

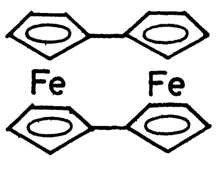
Izumi MOTOYAMA, Masanobu WATANABE, and Hirotoshi SANO
Department of Chemistry, Faculty of Science, Tokyo Metropolitan
University, Setagaya, Tokyo 158

Mixed-valence compound of diferrocenylacetylene and averaged-valence compound of [2.2]ferrocenophane-1,13-diyne were prepared by the reaction of the corresponding neutral compounds with iodine in benzene. The Mössbauer results have clearly shown that strong interactions through the conjugated π-systems between two iron atoms are present in the latter compound.

The mixed-valence cations of biferrocene I and biferrocenylene II have extensively been investigated by Cowan et al1) and Hendrickson et al2) by using Mössbauer spectroscopy and other physical measurement. It was reported on the Mössbauer spectra of these mixed-valence compounds that the former cation has the iron atoms in both the states of Fe(II) and Fe(III), whereas the latter shows a valence state averaged over Fe(II) and Fe(III). In the cource of the Mössbauer spectroscopic studies on ferrocene derivatives, we have observed interesting phenomena that the mixed-valence cations of acetylenic compounds, such as diferrocenylacetylene III and [2.2]ferrocenophane-1,13-diyne IV, show the Mössbauer spectra similar to those observed for the compounds I and II. Although the similarity between the acetylenic compounds and the biferrocene-type compounds in solution was found in the recent electrochemical investigation,3) there has been no report on the comparison of these isolated acetylenic compounds and their cationic species. In this paper, we report on the ^{57}Fe Mössbauer results for the mixed- and averaged-valence acetylenic compounds.



I



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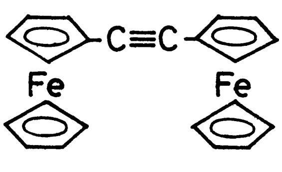

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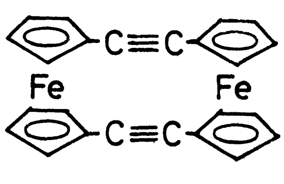
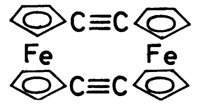
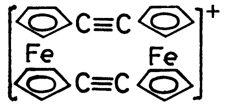
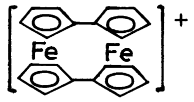


IV

Diferrocnylacetylene III and [2.2]ferrocenophane-1,13-diyne IV were prepared according to the method previously reported4) and led to the corresponding cations by the action of iodine on them in benzene. All the compounds used in this study were identified by means of their elemental analyses and the compound IV was also identified by means of its mass spectrum. Iron-57 Mössbauer measurements were carried out by using a ^{57}Co(Pt) source moving in a constant acceleration mode at room temperature. The velocity scale was normalized with respect to metallic iron. The Mössbauer parameters in units of mms^{-1} have an estimated error of not more than 0.02 mms^{-1}. Mössbauer parameters of the ferrocene derivatives obtained in this study are listed in Table 1, together with those of biferrocenium and biferrocenylenium picrates[1].

Table 1. Mössbauer parameters of ferrocene and related compounds

Compound	Temp.(K)	QS(mms^{-1})	IS(mms^{-1})
FcH	78	2.39	0.52
$[FcH]^+ I_3^-$	78	0.00	0.53
picrate$^-$	78	0.00	0.54
BF_4^-	78	0.09	0.58
FcC≡CH	78	2.34	0.49
FcC≡CCu	78	2.31	0.52
$(C_5H_4C{\equiv}CH)(C_5H_4I)Fe$	78	2.40	0.49
$(C_5H_4C{\equiv}CCu)(C_5H_4I)Fe$	78	2.34	0.52
FcC≡CFc	78	2.41	0.50
FcC≡CC≡CFc	78	2.32	0.52
	78	2.41	0.56
$[FcC{\equiv}CFc]^+ I_3^-$	78	2.18	0.54
		0.49	0.50
 I_5^-	78	1.61	0.54
	4.2	1.59	0.54
$[FcFc]^+$ picrate$^-$ *	78	2.141	0.510
		0.288	0.518
 picrate$^-$ *	78	1.780	0.525

* Reference 1. Fc: ferrocenyl.

Mössbauer parameters are generally quite different for most Fe(II) and Fe(III) compounds, but isomer shifts for ferrocene analogues are very similar to those for the corresponding ferricinium analogues. On the other hand, ferrocene has a large quadrupole splitting value, while ferricinium ion has only a vanishingly small one. Therefore, the nature of the mixed-valence compounds can be reflected in the quadrupole splitting parameter. The Mössbauer spectrum of triiodide salt of monooxidized diferrocenylacetylene, as shown in Fig. 1, has two quadrupole split doublets, the outer of which has a quadrupole splitting of 2.18 mms^{-1} centered at 0.54 mms^{-1} and the inner of which a splitting of 0.49 mms^{-1} centered at 0.50 mms^{-1}. This spectrum has a close resemblance to that of the biferrocenium cation. On the other hand, the mixed-valence cation of [2.2]ferrocenophane-1,13-diyne IV has only one quadrupole split doublet (QS: 1.61 mms^{-1}; IS: 0.54 mms^{-1} at 78 K), as also illustrated in Fig. 1, which is similar to that observed for biferrocenylenium cation. As is seen in Table 1, the Mössbauer parameters for the substituted ferrocene derivatives are essentially identical with those of ferrocene itself and the parameters for the ferricinium salts are not affected by the variation of the counter ions. Mössbauer spectroscopic studies under an external magnetic field clarified that the sign of the electric field gradient tensor for ferrocene is positive and the e_{2g} electrons have predominant contributions to the electric field gradient at the iron nucleus of ferrocene.5) Accordingly, extremely small quadrupole splitting values for ferricinium species are attributed to the loss of an e_{2g} electron from ferrocene. The quadrupole splittings of the partially oxidized acetylenic compounds are quite different from those expected for the structures having fixed Fe(II) and Fe(III) states. The fact that the Mössbauer spectrum of partially oxidized diferrocenylacetylene shows two quadrupole doublets corresponding to those of Fe(II) and Fe(III) clearly indicates that intramolecular electron-transfer from one iron to another takes place in the mixed-valence compounds with the rate of electron-transfer not exceeding 10^7 sec^{-1} in solid. In contrast to this, the Mössbauer spectrum of [2.2]ferrocenophane-1,13-diyne monocation shows only one doublet, which indicates the presence of iron atoms in the same oxidation states on the Mössbauer time scale. The quadrupole splitting value of 1.61 mms^{-1}, which is quite similar to the value of 1.78 mms^{-1} for biferrocenylene monocation, is an intermediate one between that of ferrocene and ferricinium ion. This observation clearly shows that there are strong interactions through the conjugated π-systems between the iron atoms in different formal oxidation states in this monocation inspite of its large iron-iron distances (about 6.5 A).

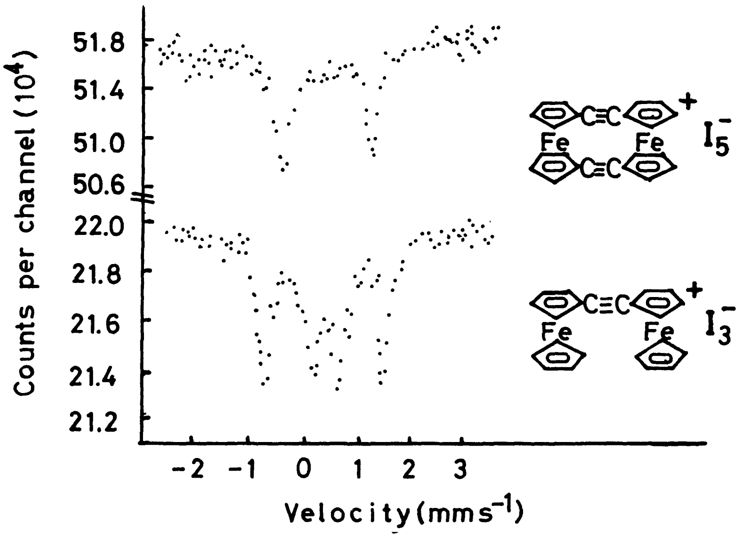


Fig. 1. Mössbauer spectra at 78 K of (a) diferrocenylacetylenium triiodide and (b) [2.2]ferrocenophane-1,13-diynium quinquiiodide. Velocity scale is shown with respect to metallic iron.

Mixed-valence compounds generally have characteristic absorption in the near infrared region,$^{1,6)}$ where neither ferrocene nor ferricinium ion has any absorption. This absorption is assigned to an intervalence electron-transfer, $[Fe(II)\text{-}Fe(III)]^+ \longrightarrow [Fe(III)\text{-}Fe(II)]^+$. All the mixed-valence compounds investigated in this study also have the corresponding absorptions in the same region, as shown in Fig. 2, although diferrocenylacetylene triiodide shows the absorption peak at the wavelength 1360 nm largely shorter than the others (1800 nm) indicating much weaker intramolecular interaction between iron atoms. In the case of biferrocenylenium triiodide, the intramolecular electron-transfer is mainly attributed to the direct interaction through the overlapped e_{2g} orbitals of both iron atoms because of its short distance (3.98 A) between them. On the basis of results presented above, however, it seems reasonable to conclude that a strong averaging effect on the oxidation states in monocationic species of [2.2]ferrocenophane-1,13-diyne IV takes place through the conjugated π-systems and not through the direct interaction between the overlapped e_{2g} orbitals because of its large iron-iron distance.

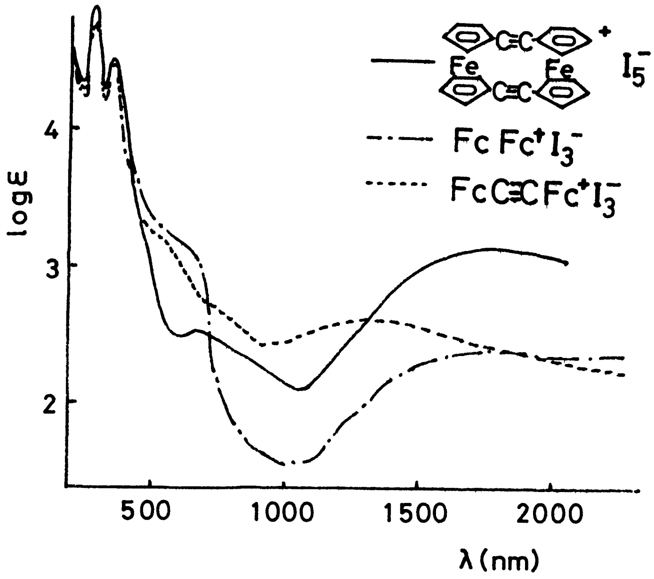


Fig. 2. Electronic spectra of biferrocenium triiodide, diferrocenylacetylenium triiodide and [2.2]ferrocenophane-1,13-diynium quinquiiodide in CH_3CN solution.

References

1) D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, Acc. Chem. Res., 6, 1 (1973); D. O. Cowan, C. LeVanda, R. L. Collins, and F. Kaufman, J. Phys. Chem., 75, 2025 (1971); D. O. Cowan, C. LeVanda, R. L. Collins, G. A. Candela, U. T. Mueller-Westerhoff, and P. Eilbracht, J. Chem. Soc. Chem. Commun., 1973, 329; C. LeVanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela, and R. L. Collins, J. Amer. Chem. Soc., 98, 3181 (1976).
2) W. H. Morrison Jr., and D. N. Hendrickson, Chem. Phys. Lett., 22, 119 (1973).
3) C. LeVanda, K. Bechgaard, and D. O. Cowan, J. Org. Chem., 41, 2700 (1976).
4) M. Rosenblum, N. M. Brawn, J. Papenmeier, and M. Applebaum, J. Organometal. Chem., 6, 173 (1966); M. Rosenblum, N. M. Brawn, D. Ciappenelli, and J. Tancrede, ibid., 24, 469 (1970).
5) R. L. Collins, J. Chem. Phys., 42, 1072 (1965).
6) D. O. Cowan, and F. Kaufman, J. Amer. Chem. Soc., 92, 219 (1970).

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