Journal of Organometallic Chemistry, 369 (1989) C33–C37
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 9985PC

Preliminary communication

Valence delocalization in mixed-valence 1′,6′-bis(*p*-halobenzyl)biferrocenium salts. A new zigzag configuration for the polyiodide ion I_5^-

Teng-Yuan Dong *, Ming-Yhu Hwang, Chi-Chang Schei,
Institute of Chemistry, Academia Sinica, Taipei, Taiwan (R.O.C.)

Shie-Ming Peng *, and Show-Kei Yeh
Department of Chemistry, National Taiwan University, Taipei, Taiwan (R.O.C.)

(Received December 20th, 1988; in revised form April 10th, 1989)

Abstract

The results of an X-ray diffraction study of 1′,6′-bis(*p*-bromobenzyl)biferrocenium pentaiodide and those of Mössbauer spectroscopy indicate that the degree of delocalization of negative charge in the triiodide unit controls the intramolecular electron transfer in mixed-valence biferrocenes.

There is considerable interest in the electron transfer process in disubstituted mixed-valence biferrocenium salts [1,2]. Very recently it has been found that the nature of the solid-state environment about a mixed-valence biferrocenium cation can dramatically affect the intramolecular electron transfer rate [3,4]. In this communication we report the new mixed-valence compound, which has zigzag polyiodide chains, and the effect of the ionic lattices on the rate of intramolecular electron transfer in the mixed-valence 1′,6′-bis(*p*-halobenzyl)biferrocenium cations.

The molecular and solid-state structure of 1′,6′-bis(*p*-bromobenzyl)biferrocenium pentaiodide (**1**) has been determined by single-crystal X-ray diffraction *. As can be seen in Fig. 1, the mixed-valence cation has a *trans* conformation; the

* Crystal data for **1**: $C_{34}H_{28}Br_2Fe_2I_5$, $M = 1342.61$, triclinic, space group $P\bar{1}$, a 9.551(3), b 10.984(3), c 11.248(5) Å, α 119.71(3), β 116.04(3), γ 76.95(3)°, U 920.74 Å^3, $Z = 1$, D_c 2.429 g cm^{-3}, $F(619) = 512.94$. Data were collected at 300 K on an Enraf–Nonius CAD4 automated diffractometer via $\theta/2\theta$ scan mode and were corrected for absorption (Mo-K_α). Of 3491 reflections collected ($2.5° < 2\theta < 49.9°$), 3246 were unique, and of these 2403 that were considered observed ($F_o > 2.5\sigma(F_o)$) were used in the solution and refinement. Weights based on counting-statistics were used. All hydrogen atoms were located and isotropically refined; non-hydrogen atoms anisotropically. $R_F = 0.052$, $R_{WF} = 0.039$.

0022-328X/89/$03.50

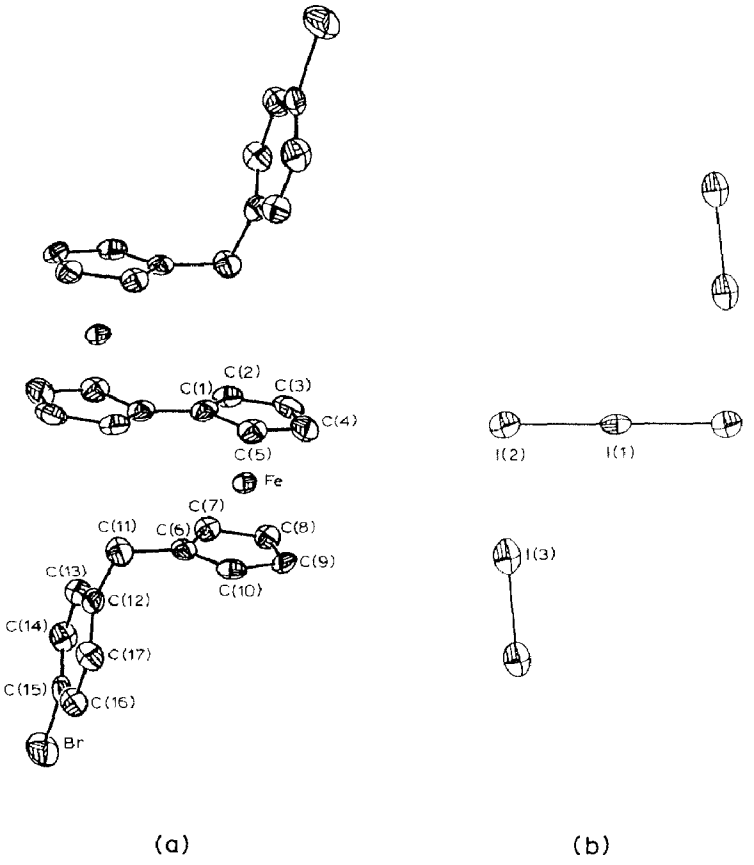

Fig. 1. ORTEP plots of 1′,6′-bis(*p*-bromobenzyl)biferrocenium cation in **1** (a) and zigzag configuration of polyiodide chain in **1** (b). Both are plotted with 50% probability ellipsoids.

two iron ions are on opposite sides of the planar fulvenide ligand. The rings of each ferrocenyl moiety are nearly parallel; the dihedral angle is 3.3°. The two rings are nearly eclipsed with an average staggering angle of 1.2(3)°. The mixed-valence cation is located at a centre of symmetry with a centroid-to-centroid distance of 3.344(1) Å, for each metallocene moiety, which is intermediate between that in Fe^{II}, 3.390 Å [1], and Fe^{III}, 3.313 Å [1]. Table 1 lists important bond distances and angles.

As viewed down the *c*-axis (Fig. 2) the solid-state structure of **1** is composed of parallel sheets of mixed-valence biferrocenium cations and polyiodide ions which contain zigzag chains of alternate I_3 and I_2 units. This unusual well-established polyiodide is not seen in the three structurally characterized biferrocenium triiodide salts [1,5]. The value of I–I distance in the centrosymmetric I_3^- ion is 2.9250(17) Å which is in accord with the standard value of 2.920 Å proposed for the free I_3^- ion [6]. The bond length in the I_2 molecule is 2.741(2) Å, significantly larger than the value of 2.68 Å found in crystalline I_2 [7]. The distance of 3.486(2) Å between neighbouring iodine atoms in I_2 and I_3^- units within a chain indicates a significant interaction, in view of the in-plane intermolecular distance of 3.50 Å found in crystalline I_2 [7]. A zigzag chain of pentaiodide has also been observed in the complex of $(phenacetin)_2 \cdot HI_5$ in which the $I_3^- \cdots I_2$ distance is 3.550(2) Å [8]. The

Table 1

Selected bond lengths (Å) and bond angles (deg) for **1**

Bond lengths			
I(1)–I(2)	2.9250(17)	C(6)–C(7)	1.416(9)
I(1)–I(2) [a]	2.9250(17)	C(6)–C(10)	1.412(10)
I(3)–I(3) [b]	2.7406(17)	C(6)–C(11)	1.497(10)
Br–C(15)	1.909(7)	C(7)–C(8)	1.412(10)
C(8)–C(9)	1.416(10)	C(9)–C(10)	1.422(10)
C(11)–C(12)	1.518(10)	C(12)–C(13)	1.384(11)
C(1)–C(1) [c]	1.446(13)	C(12)–C(17)	1.365(10)
C(1)–C(2)	1.438(10)	C(13)–C(14)	1.387(11)
C(1)–C(5)	1.432(10)	C(2)–C(3)	1.404(11)
C(14)–C(15)	1.366(11)	C(3)–C(4)	1.426(12)
C(15)–C(16)	1.386(12)	C(4)–C(5)	1.417(11)
Bond angles			
I(2)–I(1)–I(2) [a]	180.0	C(3)–C(4)–C(5)	108.7(7)
C(1)–C(5)–C(4)	106.9(6)	C(7)–C(6)–C(10)	107.3(6)
C(7)–C(6)–C(11)	125.0(6)	C(10)–C(6)–C(11)	127.7(6)
C(6)–C(7)–C(8)	108.4(6)	C(7)–C(8)–C(9)	108.4(6)
C(8)–C(9)–C(10)	107.0(6)	C(6)–C(10)–C(9)	108.9(6)
C(6)–C(11)–C(12)	109.0(5)	C(11)–C(12)–C(13)	119.5(6)
C(11)–C(12)–C(17)	121.6(7)	C(1) [c]–C(1)–C(2)	125.5(6)
C(13)–C(12)–C(17)	118.6(6)	C(1) [c]–C(1)–C(5)	125.7(6)
C(12)–C(13)–C(14)	121.1(7)	C(2)–C(1)–C(5)	108.4(6)
C(13)–C(14)–C(15)	118.2(7)	C(1)–C(2)–C(3)	107.4(6)
Br–C(15)–C(14)	119.3(6)	Br–C(15)–C(16)	118.4(6)
C(14)–C(15)–C(16)	122.3(7)	C(15)–C(16)–C(17)	117.6(7)
C(2)–C(3)–C(4)	108.6(6)	C(12)–C(17)–C(16)	122.1(7)

[a] The following atoms are the equivalents: I(2) $-x\ -y\ -z$. [b] I(3) $-x\ 1-y\ 1-z$. [c] C(1) $-x\ 2-y\ 1-z$.

positioning of the I_3^- anion relative to the mixed-valence cation in **1** apparently is also unusual (Fig. 2). The I_3^- moiety in **1** is parallel to the fulvenide ligand, rather than perpendicular to the fulvenide ligand as found in biferrocenium and 1′,6′-disubstituted biferrocenium triiodide salts [1,2]. Furthermore, Br- - -I contacts be-

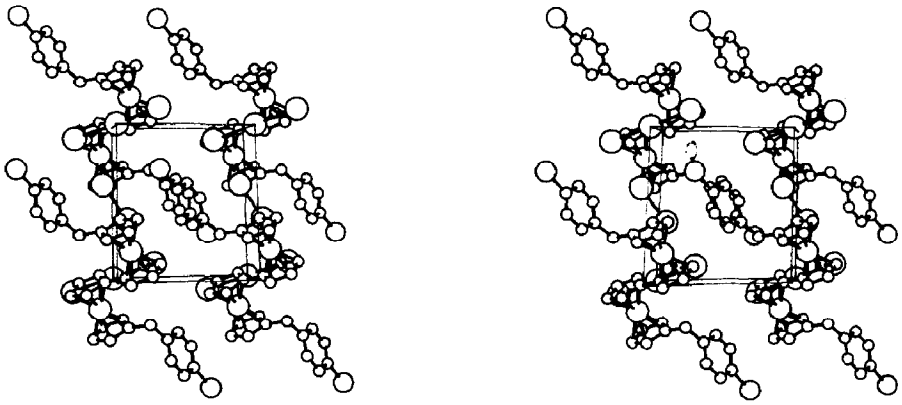

Fig. 2. Stereoview of the packing arrangement of **1**, as viewed down the *c*-axis.

tween the cation and anion in the range of 3.866(2)–4.180(2) Å were noted in the structure.

In agreement with the structural characterization we have found that a sample of **1** at 298 K gives a Mössbauer spectrum with one quadrupole-split doublet (ΔE_Q 1.098 mm/s). This pattern of one doublet is what is expected for a valence delocalized biferrocenium cation (electron transfer rate greater than the time scale of Mössbauer technique, i.e., $> 10^7\ s^{-1}$) [1,2]. However, the Mössbauer spectrum of 1′,6′-bis(*p*-chlorobenzyl)biferrocenium triiodide (**2**) is quite different from what is seen for compound **1**. By a least-squares fit to Lorentzian line shapes, the features in the 300 K spectrum of **2** are two doublets, one with a ΔE_Q of 0.776 mm/s and the other with ΔE_Q 1.394 mm/s. Furthermore, both doublets have the same area, which clearly indicates that compound **2** is valence trapped on the Mössbauer time scale (electron transfer rate is less than $\sim 10^7\ s^{-1}$).

Room-temperature IR spectra were also run for KBr pellets of unoxidized 1′,6′-bis(*p*-bromobenzyl)biferrocene. The C–H bending mode of Cp groups for the unoxidized biferrocene is at 810 cm^{-1}. Two bands at 818 cm^{-1} and 832 cm^{-1} are observed for **1**. If the band at 832 cm^{-1} can be assigned to the C–H bending mode associated with the Fe^{III} moiety, then **1** is localized on the IR time scale.

The Mössbauer data clearly indicate that the intramolecular electron transfer rate in **1** is greater than $\sim 10^7\ s^{-1}$, whereas the rate for **2** is less than $\sim 10^7\ s^{-1}$. This difference does not originate in a difference in electronic or vibrational coupling in **1** and **2**. Evidence in support of the statement that the electronic coupling within the cations of **1** and **2** is probably not different in either can be gleaned from the electrochemical data for the two neutral biferrocenes. Each shows two one-electron oxidation waves, and the separation between the two one-electron oxidation waves is the same. The difference of electron transfer rates for **1** and **2** can be explained by the degree of delocalization of negative charge in the I_3^- unit. In the solid-state the environment about the mixed-valence cation influences the rate of intramolecular electron transfer. For compound **2**, which shows a moderate electronic coupling between the metal centers, the anion has to interconvert rapidly between two configurations, one which is the limiting form: $I_A^- \cdots I_B\text{–}I_C$, and the other is described as $I_A\text{–}I_B \cdots I_C^-$, so that it does not limit the rate of electron transfer. In the case of **1**, we suggest that the zigzag polyiodide chain has greater delocalization of negative charge so that it does not limit the rate of intramolecular electron transfer.

Supplementary material available

Tables of experimental and crystal data (Table s1, 1 page) atomic coordinates (Table s2, 2 pages), anisotropic thermal parameters (Table s3, 2 pages), bond distances and angles (Table s4, 5 pages), and a listing of structure factors (15 pages) are available from the authors.

Acknowledgement. We thank the National Science Council for support (to T.-Y.D. and S.M.P.).

References

1 T.-Y. Dong, D.N. Hendrickson, K. Iwai, M.J. Cohn, A.L. Reingold, H. Sano, I. Motoyama, and S. Nakashima, J. Am. Chem. Soc., 107 (1985) 7996.

2 T.-Y. Dong, D.N. Hendrickson, C.G. Pierpont, and M.F. Moore, J. Am. Chem. Soc., 108 (1986) 963.
3 T.-Y. Dong, T. Kambara, and D.N. Hendrickson, J. Am. Chem. Soc., 108 (1986) 4423.
4 T.-Y. Dong, T. Kambara, and D.N. Hendrickson, J. Am. Chem. Soc., 108 (1986) 5857.
5 S. Iijima, R. Saida, I. Motoyama, and H. Sano, Bull. Chem. Soc., Japan, 54 (1981) 1375.
6 J. Runsink, S. Swen-Walstra, and T. Migchelsen, Acta Cryst. B, 28 (1972) 1331.
7 A.I. Kitaigorodskii, T.L. Khotsyanova, and Y.T. Struchkov, Zh. Fiz. Khim., 27 (1953) 780.
8 F.H. Herbstein and M. Kapon, Nature Phys. Sci., 239 (1972) 153.