

C16	-0.2568 (3)	0.2913 (4)	-0.3635 (3)	3.4 (1)
C17	-0.1801 (3)	0.1617 (4)	-0.1310 (3)	3.2 (1)
C18	-0.0892 (3)	0.1858 (4)	-0.0710 (3)	3.0 (1)
O19	0.0178 (3)	0.4393 (3)	0.3928 (3)	5.4 (1)
C20	0.0857 (4)	0.3845 (6)	0.3666 (5)	6.7 (2)
O21	0.0854 (6)	0.0863 (7)	0.1578 (6)	10.2 (2)
O22	-0.032 (1)	0.157 (2)	0.308 (1)	9.0 (5)

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Table 2. Selected geometric parameters (Å, °)

Fe...Fe ⁱ	3.188 (1)	Fe—O10	2.082 (3)
Fe—O3	1.830 (2)	Fe—N	2.246 (4)
Fe—O4	2.005 (3)	O4—C12	1.298 (4)
Fe—O6	2.025 (3)	O5—C12	1.240 (8)
Fe—O8	2.020 (3)	O11...O21	2.924 (9)
O3—Fe—O4	98.7 (1)	N—Fe—O3	175.4 (1)
O3—Fe—O6	95.5 (1)	N—Fe—O4	85.6 (1)
O3—Fe—O8	103.8 (1)	N—Fe—O6	80.1 (1)
O3—Fe—O10	102.5 (1)	N—Fe—O8	77.8 (1)
O4—Fe—O6	165.5 (1)	N—Fe—O10	76.4 (1)
O4—Fe—O8	88.1 (1)	Fe—O3—Fe ⁱ	121.1 (2)
O4—Fe—O10	86.9 (1)	Fe—O4—C12	122.4 (3)
O6—Fe—O8	91.4 (1)	O4—C12—O5	120.2 (3)
O6—Fe—O10	87.2 (1)	O4—C12—O4 ⁱ	119.7 (5)
O8—Fe—O10	154.0 (1)		

Symmetry code: (i) $-x, y, -z - \frac{1}{2}$.

Laue group 2/m and systematic absences, hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$, indicated the space group Cc (No. 9) or $C2/c$ (No. 15). Assuming the space group to be $C2/c$, the position of the Fe atom was obtained by direct methods and the other non-H atoms were located from Fourier syntheses. All the H atoms of the complex ion were located from difference syntheses, as were the methanol and water molecules of crystallization, but their H atoms were not included in the refinement. The water molecule is disordered and the site occupation ratio of two possible positions, O20 and O21, was estimated at 7:3 from the isotropic displacement parameters. Calculations were carried out using *CRYSTAN-GM* software (MAC Science, 1992) on a SUN SPARC2 workstation at Keio University.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71620 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1044]

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Structural Characterization of Mixed-Valence 1',2',1''',2'''-Tetraethylbiferrocenium Triiodide

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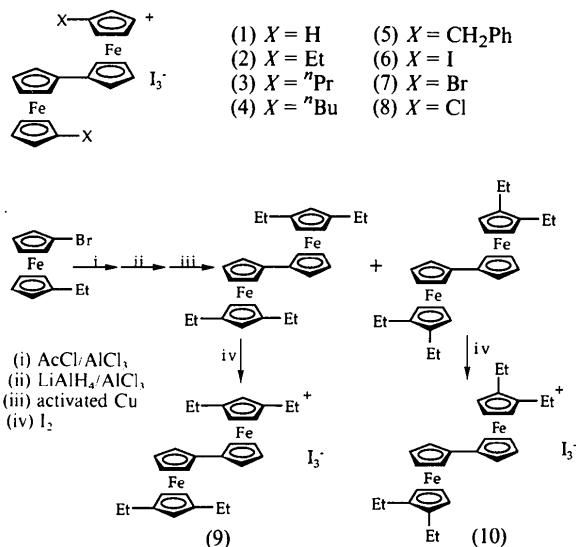
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Abstract

The structure determination of the title compound $\{\mu-1(\eta^5):2(\eta^5)-1,1'$ -bicyclopentadienyldiyl-bis[1,2-(η^5)-1,2-diethylcyclopentadienyl]diiron(II,III) triiodide chlorobenzene solvate, $[\text{Fe}_2(\text{C}_9\text{H}_{13})_2(\text{C}_{10}\text{H}_8)(\text{I}_3)\cdot\text{C}_6\text{H}_5\text{Cl} (10)]\}$ indicates that this mixed-valence cation has a valence-trapped electronic state.

Comment

Studies of electron transfer in mixed-valence biferrocenium complexes [(1)–(8)] have revealed that the environment around a given mixed-valence molecule is the most important factor in determining the rate of intramolecular electron transfer (Hammack, Drickamer, Lowery & Hendrickson, 1988; Sinha, Lowery, Ley, Drickamer & Hendrickson, 1988; Webb, Geib, Staley, Rheingold & Hendrickson, 1990; Dong, Kambara & Hendrickson, 1986; Dong, Hendrickson, Iwai, Cohn, Geib, Rheingold, Motoyama & Nakashima, 1985). A recent finding of interest is that there is a correlation between the dihedral angle of the Cp rings for a given ferrocenyl moiety and the rate of electron transfer, *i.e.* the larger the dihedral angle, the faster the electron transfer (Dong & Chou, 1990; Dong, Chang, Huang, Wen, Lee, Chen, Yeh & Yeh, 1992; Dong, Lee & Lin, 1992). In a previous communication (Dong *et al.*, 1992), we reported that there is a dramatic difference in electron-transfer rates between complexes (9) and (10), which were prepared by



adding a stoichiometric amount of I₂ to a benzene/hexane (1:1) solution of the corresponding biferrocene at 273 K. At temperatures below 100 K, each shows two doublets in Mössbauer spectra, one representing the Fe^{II} site and the other the Fe^{III} site. An increase in temperature in each case causes the two doublets to move together with no discernible line broadening, to eventually become a single 'average-valence' doublet at temperatures of 125 and 195 K for (9) and (10), respectively. In contrast to compound (9), a more crystalline sample of (10) prepared by slowly diffusing hexane into a CH₂Cl₂ or chlorobenzene solution containing compound (10) gives Mössbauer spectra with localized (two doublets) and delocalized (one average doublet) spectra superimposed. Examination of the 77 K spectrum reveals that it consists of valence-trapped (Fe^{II}, $\Delta E_Q = 1.882 \text{ mm s}^{-1}$; Fe^{III}, $\Delta E_Q = 0.499 \text{ mm s}^{-1}$) and valence-detrapped (Fe^{II/III}, $\Delta E_Q = 1.118 \text{ mm s}^{-1}$) signals. As the temperature is increased, the intensity of the detrapped signal grows at the expense of the trapped signal. The ratio of valence-localized to valence-delocalized species changes from 1:0.22 to 1:1.13 as the temperature is increased from 77 to 300 K. In this communication, the results of X-ray structural work for localized species of (10) are presented.

Compound (10) exhibits two crystal morphologies (needles and plate-like crystals) at room temperature; the needle form is suitable for single-crystal X-ray determination. An ORTEPII (Johnson, 1976) plot of the cation and anion is given in Fig. 1. There is no crystallographic symmetry imposed on the cations and anions. The dihedral angles between the two five-membered rings associated with Fe(1) and Fe(2) are 3.4 (7) and 3.8 (7)°, respectively. Furthermore, the two Cp rings of the fulvalenide ligand are not

coplanar; they form a dihedral angle of 9.5 (7)°. Each pair of Cp rings in the Fe(1) and Fe(2) moieties are nearly eclipsed with average staggered angles of 0.7 (1) and 3.6 (1)°, respectively. The average distances of iron to the Cp centres are 1.667 (7) and 1.678 (7) Å for the Fe(1) and Fe(2) metallocenes, respectively. The I₃⁻ anion is also unsymmetrical, with distances I(1)—I(2) = 2.879 (2) and I(1)—I(3) = 2.966 (2) Å. The I₃⁻ anion possesses I₂I⁻ character, where the I(3) atom probably carries more negative charge than the other terminal I(2) atom. The single-crystal determination indicates that this mixed-valence cation has a localized electronic state.

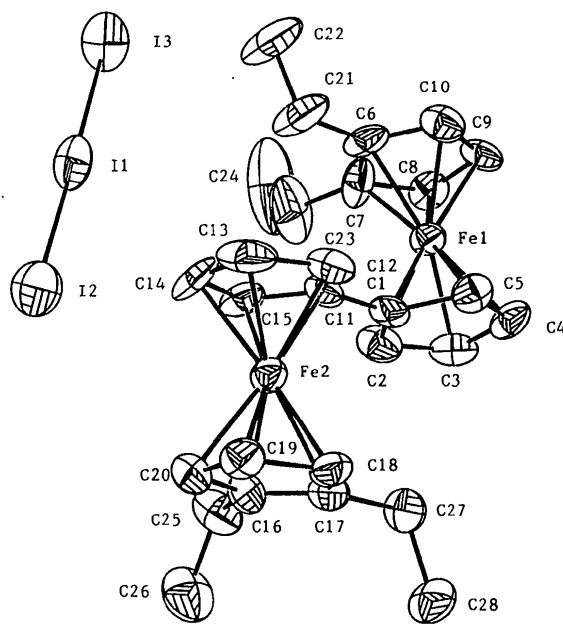
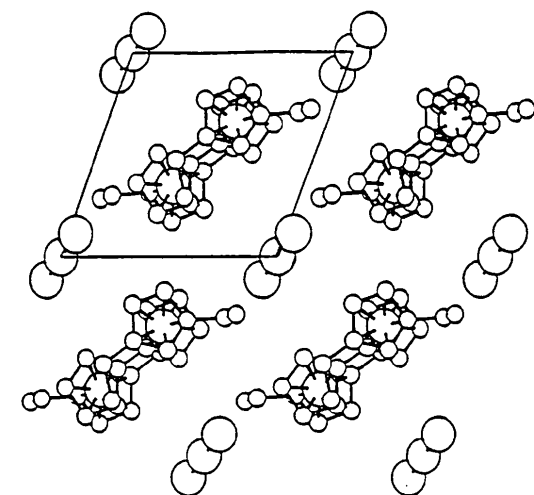


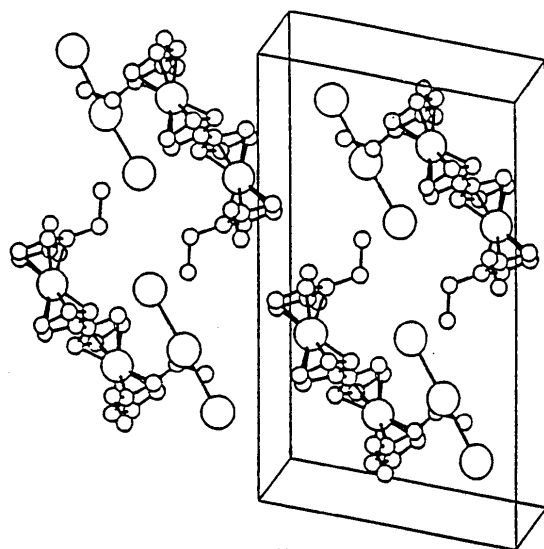
Fig. 1. ORTEPII (Johnson, 1976) plot of (10).

An interesting finding is that the two ethyl substituents on the Cp ring are perpendicular to the fulvalenide ligand; this is in contrast to their positions in compound (9) in which one ethyl substituent is parallel to the fulvalenide ligand while the other is perpendicular to it. Consequently, the packing arrangement of the cations and anions in (10) is different from that in (9) (Fig. 2). The packing arrangement in (10) can be described as consisting of step-like columns. However, compound (9) has a layer structure. Three-dimensional hydrogen bonding is clearly observed between the H and I atoms. The closest contact is 3.18 Å. There is also a hydrogen-bond network between the ethyl groups and I₃⁻ anions. It has been suggested that the hydrogen-bond networks in the series of mixed-valence biferrocenium salts play an important role in determining the rate of electron transfer (Konno & Sano, 1988).

We believe that the hydrogen-bond networks play an important role in tilting the Cp rings from parallel geometry. Consequently, the tilting of the Cp rings has a pronounced influence on the rate of electron transfer. Detailed and systematic studies are in progress.



(a)



(b)

Fig. 2. Packing arrangement of (a) (9) as viewed down the c axis and (b) (10) as viewed down the x axis.

Experimental

Compound (10) was prepared as described in the *Comment*. A crystal was obtained when a layer of hexane was allowed to slowly diffuse into a chlorobenzene solution of the title compound.

Crystal data

$[\text{Fe}_2(\text{C}_9\text{H}_{13})_2(\text{C}_{10}\text{H}_8)](\text{I}_3) \cdot \text{C}_6\text{H}_5\text{Cl}$

$M_r = 975.43$

Triclinic

$P\bar{1}$

$a = 8.235$ (3) Å

$b = 11.152$ (4) Å

$c = 18.442$ (5) Å

$\alpha = 100.597$ (25)°

$\beta = 102.100$ (24)°

$\gamma = 96.89$ (3)°

$V = 1605.4$ (9) Å³

$Z = 2$

$D_x = 2.018$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25 reflections

$\theta = 7.67$ – 14.89 °

$\mu = 3.78$ mm⁻¹

$T = 298$ K

Needle

$0.31 \times 0.19 \times 0.16$ mm

Black

Data collection

Enraf-Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction: empirical (ψ rotation)

$T_{\min} = 0.834$, $T_{\max} = 0.999$

6077 measured reflections

5643 independent reflections

2253 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 24.9$ °

$h = 0 \rightarrow 9$

$k = -13 \rightarrow 13$

$l = -21 \rightarrow 21$

3 standard reflections

frequency: 60 min

intensity variation: 10%

Refinement

Refinement on F

$R = 0.048$

$wR = 0.049$

$S = 1.52$

2253 reflections

318 parameters

$w = 1/[\sigma^2(F_o) + 0.00005(F_o)^2]$

$(\Delta/\sigma)_{\max} = 0.242$

$\Delta\rho_{\max} = 0.63$ e Å⁻³

$\Delta\rho_{\min} = -0.56$ e Å⁻³

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*$$

	x	y	z	B_{eq}
I(1)	0.97588 (15)	0.71020 (11)	0.30234 (7)	6.16 (6)
I(2)	0.98028 (18)	0.57918 (13)	0.42326 (8)	8.10 (8)
I(3)	0.97895 (18)	0.84082 (12)	0.17622 (8)	7.84 (8)
Fe(1)	0.2067 (3)	0.35798 (17)	0.15548 (10)	3.02 (9)
Fe(2)	0.5399 (2)	0.14128 (17)	0.34381 (10)	3.00 (10)
C(1)	0.2836 (19)	0.2543 (12)	0.2355 (7)	3.2 (7)
C(2)	0.234 (2)	0.3640 (14)	0.2707 (8)	4.2 (8)
C(3)	0.060 (2)	0.3593 (14)	0.2342 (8)	4.5 (9)
C(4)	0.0067 (16)	0.2509 (14)	0.1762 (8)	4.0 (8)
C(5)	0.1456 (18)	0.1853 (11)	0.1751 (7)	3.5 (7)
C(6)	0.4023 (19)	0.4152 (16)	0.1091 (9)	4.4 (9)
C(7)	0.3487 (18)	0.5181 (14)	0.1482 (9)	4.8 (9)
C(8)	0.1761 (18)	0.5101 (12)	0.1126 (8)	3.7 (8)
C(9)	0.1249 (19)	0.4049 (13)	0.0529 (7)	3.8 (8)
C(10)	0.268 (2)	0.3441 (14)	0.0517 (8)	4.4 (8)
C(11)	0.4531 (18)	0.2255 (13)	0.2534 (7)	3.1 (7)
C(12)	0.5016 (19)	0.1075 (13)	0.2272 (7)	4.0 (8)
C(13)	0.677 (2)	0.1159 (17)	0.2623 (9)	5.2 (10)
C(14)	0.7316 (17)	0.2326 (15)	0.3104 (9)	4.5 (9)
C(15)	0.5961 (18)	0.3001 (12)	0.3055 (8)	3.8 (8)
C(16)	0.4832 (17)	0.1929 (12)	0.4488 (7)	3.3 (7)
C(17)	0.3467 (18)	0.1064 (13)	0.4009 (7)	3.2 (7)
C(18)	0.4056 (17)	-0.0040 (13)	0.3743 (7)	3.6 (7)
C(19)	0.5816 (17)	0.0133 (12)	0.4090 (8)	3.5 (7)

C(20)	0.6308 (18)	0.1329 (14)	0.4547 (7)	4.0 (8)
C(21)	0.580 (2)	0.3850 (17)	0.1258 (10)	6.9 (11)
C(22)	0.685 (2)	0.444 (2)	0.0798 (11)	8.6 (13)
C(23)	0.450 (3)	0.6187 (17)	0.2123 (11)	8.8 (12)
C(24)	0.480 (3)	0.733 (2)	0.2048 (16)	15.0 (19)
C(25)	0.4844 (19)	0.3213 (14)	0.4904 (8)	5.1 (9)
C(26)	0.485 (2)	0.3301 (15)	0.5713 (9)	6.4 (10)
C(27)	0.1652 (17)	0.1242 (13)	0.3786 (8)	4.1 (8)
C(28)	0.0666 (17)	0.0755 (15)	0.4299 (8)	5.0 (9)
Cl	0.263 (2)	0.9059 (14)	0.0276 (8)	17.0 (5)
C(31)	0.411 (5)	0.984 (4)	0.004 (2)	7.2 (10)
C(32)	0.406 (3)	1.0464 (19)	-0.0410 (11)	7.3 (5)
C(33)	0.479 (6)	0.897 (3)	0.051 (2)	7.0 (9)
C(34)	0.263 (4)	0.993 (3)	-0.0180 (17)	4.8 (7)

Table 2. Selected geometric parameters (Å, °)

I(1)—I(2)	2.879 (2)	C(6)—C(21)	1.52 (2)
I(1)—I(3)	2.966 (2)	C(7)—C(8)	1.42 (2)
Fe(1)—C(1)	2.080 (12)	C(7)—C(23)	1.49 (2)
Fe(1)—C(2)	2.077 (13)	C(8)—C(9)	1.41 (2)
Fe(1)—C(3)	2.072 (14)	C(9)—C(10)	1.43 (2)
Fe(1)—C(4)	2.060 (13)	C(11)—C(12)	1.45 (2)
Fe(1)—C(5)	2.048 (12)	C(11)—C(15)	1.41 (2)
Fe(1)—C(6)	2.064 (14)	C(12)—C(13)	1.44 (2)
Fe(1)—C(7)	2.057 (14)	C(13)—C(14)	1.40 (3)
Fe(1)—C(8)	2.020 (12)	C(14)—C(15)	1.42 (2)
Fe(1)—C(9)	2.054 (12)	C(16)—C(17)	1.408 (19)
Fe(1)—C(10)	2.063 (14)	C(16)—C(20)	1.45 (2)
Fe(2)—C(11)	2.100 (12)	C(16)—C(25)	1.49 (2)
Fe(2)—C(12)	2.062 (12)	C(17)—C(18)	1.42 (2)
Fe(2)—C(13)	2.061 (14)	C(17)—C(27)	1.512 (19)
Fe(2)—C(14)	2.040 (13)	C(18)—C(19)	1.430 (19)
Fe(2)—C(15)	2.061 (12)	C(19)—C(20)	1.40 (2)
Fe(2)—C(16)	2.081 (13)	C(21)—C(22)	1.51 (2)
Fe(2)—C(17)	2.121 (14)	C(1)—C(2)	1.42 (2)
Fe(2)—C(18)	2.081 (13)	C(1)—C(5)	1.438 (19)
Fe(2)—C(19)	2.043 (12)	C(1)—C(11)	1.45 (2)
Fe(2)—C(20)	2.048 (12)	C(2)—C(3)	1.44 (2)
C(3)—C(4)	1.41 (2)	C(23)—C(24)	1.31 (3)
C(4)—C(5)	1.43 (2)	C(25)—C(26)	1.48 (2)
C(6)—C(7)	1.41 (3)	C(27)—C(28)	1.50 (2)
C(6)—C(10)	1.40 (2)		
I(2)—I(1)—I(3)	178.27 (6)	C(7)—C(8)—C(9)	109.8 (13)
C(1)—C(2)—C(3)	106.7 (13)	C(8)—C(9)—C(10)	106.9 (12)
C(1)—C(5)—C(4)	107.0 (12)	C(11)—C(12)—C(13)	107.4 (13)
C(1)—C(11)—C(12)	125.5 (12)	C(11)—C(15)—C(14)	108.7 (13)
C(1)—C(11)—C(15)	127.2 (12)	C(12)—C(11)—C(15)	106.9 (12)
C(2)—C(1)—C(5)	109.1 (13)	C(12)—C(13)—C(14)	107.8 (13)
C(2)—C(1)—C(11)	124.4 (13)	C(13)—C(14)—C(15)	109.1 (13)
C(2)—C(3)—C(4)	109.0 (13)	C(16)—C(17)—C(18)	109.0 (12)
C(3)—C(4)—C(5)	108.3 (12)	C(16)—C(20)—C(19)	107.6 (12)
C(5)—C(1)—C(11)	126.2 (13)	C(17)—C(16)—C(20)	107.3 (12)
C(6)—C(7)—C(8)	105.9 (13)	C(17)—C(18)—C(19)	107.2 (12)
C(6)—C(10)—C(9)	107.4 (13)	C(18)—C(19)—C(20)	108.8 (12)
C(7)—C(6)—C(10)	110.1 (13)		

A three-dimensional Patterson synthesis was used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-H atoms from Fourier synthesis. The chlorobenzene is found to be positionally disordered with two sites in the population ratio 50:50. The two sites are related to each other by a symmetry centre. All non-H atoms were refined anisotropically. During the final cycles of refinement, fixed H-atom contributions with C—H bond lengths fixed at 1.08 Å were applied. *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) was used for computations.

We thank the National Science Council for financial support.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71657 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1046]

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