

BIFERROCENIUM TETRABROMOFERRATE, [(C₅H₅)Fe(C₅H₄)-(C₅H₄)Fe(C₅H₅)]FeBr₄. THE X-RAY STRUCTURAL CHARACTERIZATION OF A MIXED-VALENCE COMPOUND

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Summary

Biferrocenium tetrabromoferrate, [(C₅H₅)Fe(C₅H₄)-(C₅H₄)Fe(C₅H₅)]FeBr₄ (1) obtained as a by-product in the synthesis of biferrocenium trihalide salts, crystallizes in the noncentrosymmetric orthorhombic space group, *P*2₁2₁2₁: (at 296 K) *a* 7.492(2), *b* 9.903 (2), *c* 31.604(9) Å, *V* 2345(1) Å³, and *Z* = 4. The cation, similar to other structurally characterized biferrocenium salts, adopts a *trans*-configuration, but, in contrast, possesses no crystallographically imposed symmetry relating the two ferrocenyl environments. Different average Fe–ring distances at the two environments: Fe(1), 2.02(2) and Fe(2), 2.08(2) Å are typical of iron(II) and iron(III) states, respectively, indicating the presence of trapped oxidation states. Interionic contacts are both shorter and more numerous for the iron(III) ferrocenyl fragment than for the iron(II) fragment. Both ferrocenyl units have non-eclipsed ring configurations, with a staggering angle of 6.5(3)° at Fe(1) and 23.5(3)° at Fe(2). The FeBr₄[−] counterion is tetrahedral and ordered.

Introduction

Interest in the electron transfer process in systems where a considerable distance separates the donor and acceptor sites has been very recently focused on mixed valence, Fe^{II}–Fe^{III}, biferrocenium salts [1,2]. The results from the three structurally characterized biferrocenium triiodide salts, [(RC₅H₄)(C₅H₄)Fe]₂I₃ (2, R = H, [1,2]; 3, R = n-propyl [3] and 4, R = n-butyl [2]) show a structural equivalence in Fe sites at room temperature, but different Fe environments below 200 K; these conclusions are supported by variable-temperature Mössbauer spectroscopy data [1–3]. In the

course of preparing mixed-halogen, biferrocenium trihalide salts, a by-product, biferrocenium tetrabromoferrate $[(C_5H_5)(C_5H_4)Fe]_2FeBr_4$ (**1**) was prepared, and provided an opportunity to examine the structure of a biferrocenium salt with an anion other than triiodide. Whereas crystallographically imposed inversion centers in the room-temperature structures of **2–4** create equivalency in the two Fe centers, **1** crystallizes without restriction. The imposed symmetry for **2** requires the presence of disorder in the Fe coordination spheres (and in the anion as well) to accommodate the different Fe–ring distances for the two oxidation states (about 0.04 Å). Additionally, **1**, containing the isotropic tetrahedral $FeBr_4^-$ counterion, would be less susceptible to anion distortion (disorder) than I_3^- which can adopt an I_2-I^- structure [2].

Experimental

Synthesis

A sample of biferrocene was prepared as described previously [2]. The crystal of **1** used in the present study resulted from attempts to grow crystals of biferrocenium dibromiodate, which was prepared in the following manner. A solution of 0.1 M $HIBr_2$ was prepared by mixing 1.03 g IBr and 0.81 ml aqueous 50% HBr in a 50 ml volumetric flask, and then diluting to the mark with methanol. Biferrocenium dibromiodate $(C_{20}H_{18}Fe_2)(Br_2I)$ was prepared by dissolving biferrocene and a stoichiometric amount of *p*-benzoquinone in hexane/benzene (1/2) at 0°C. To this solution a stoichiometric amount of 0.1 M $HIBr_2$ /methanol solution was added with rapid stirring. The resulting microcrystalline solid was filtered, washed with a little cold benzene, and vacuum dried. Found: C, 36.43; H, 2.60; Fe, 16.90. $C_{20}H_{18}Fe_2IBr_2$ calcd.: C, 36.58; H, 2.76; Fe, 17.01%.

A crystal of **1** was grown by diffusing hexane into a CH_2Cl_2 solution of biferrocenium dibromiodate. In the process it was always found that a large majority of the solid was amorphous. Several other crystallization techniques failed to give appreciable quantities of crystalline **1**.

Collection of diffraction data

The parameters used during the collection of diffraction data are reported in Table 1. The crystal, a thin blue-black plate ($0.02 \times 0.28 \times 0.31$ mm), was attached to a fine glass fiber with epoxy cement. The compound was found to crystallize in the orthorhombic space group $P2_12_12_1$. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $20 \leq 2\theta \leq 30$. The data were corrected for absorption by an empirical procedure which refines three parameters to fit a thin plate. Reflections making a small ($\leq 3^\circ$) glancing angle to the principal face (0,0,1), for which significant edge effect intensity distortions are expected, were discarded (201 reflections). A profile fitting procedure was applied to all intensity data to improve the precision of the measurement of weak reflections.

Solution and refinement of the structure

The structure was solved by direct methods (SOLV) which located the three Fe and four Br atoms. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically except for atoms C(4) and C(6). Hydrogen atom positions were calculated

(Continued on p. 245)

TABLE 1
CRYSTAL, DATA COLLECTION AND REFINEMENT PARAMETERS FOR $C_{20}H_{18}Fe_3Br_4$

<i>(a) Crystal parameters</i>			
Formula	$C_{20}H_{18}Fe_3Br_4$	$V, \text{\AA}^3$	2345(1)
Crystal system	orthorhombic	Z	4
Space group	$P2_12_12_1$	ρ (calcd), g cm^{-3}	2.11
$a, \text{\AA}$	7.492(2)	temp., $^{\circ}\text{C}$	23
$b, \text{\AA}$	9.903(2)	μ, cm^{-1}	91.0
$c, \text{\AA}$	31.604(9)		
<i>(b) Data collection</i>			
Diffractometer	Nicolet R3	$R(\text{int}), \%$	1.51
Radiation	Mo- K_{α} (λ 0.71073 \AA)	reflections collected	3362
Monochromator	graphite	unique data	2876
Scan technique	θ - 2θ	unique data, $3\sigma(F_0)$	1911
2θ scan range, deg	$4^{\circ} \leq 2\theta \leq 45^{\circ}$	standard reflections	3 std/197 rflns
Data collected	$\pm h, +k, +l$	decay	$\leq 1\%$
max/min transm.	0.827/0.304		
<i>(c) Refinement</i>			
$R_F, \%$	5.93	GOF	1.29
$R_{wF}, \%$	5.71	data/parameter	8.31

TABLE 2
ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U^a
Fe(1)	2516(4)	4858(3)	-306(1)	46(1)
Fe(2)	1014(4)	5482(3)	-1862(1)	54(1)
Fe(3)	233(4)	5097(3)	1434(1)	65(1)
Br(1)	-2656(4)	4732(3)	1178(1)	108(1)
Br(2)	49(4)	6157(3)	2092(1)	92(1)
Br(3)	1822(4)	3063(3)	1507(1)	100(1)
Br(4)	1705(4)	6559(3)	974(1)	87(1)
C(1)	1219(22)	5460(17)	-847(6)	38(7)
C(2)	78(27)	4729(21)	-577(7)	66(9)
C(3)	-110(26)	5430(23)	-193(7)	77(10)
C(4)	1066(26)	6612(20)	-219(7)	56(6)
C(5)	1860(28)	6619(17)	-615(6)	53(8)
C(6)	4513(29)	3555(21)	-468(7)	73(7)
C(7)	3327(33)	2980(21)	-176(9)	87(12)
C(8)	3378(29)	3765(22)	196(7)	62(9)
C(9)	4534(27)	4832(20)	138(7)	67(9)
C(10)	5205(28)	4736(22)	-300(8)	79(10)
C(11)	1933(27)	4997(19)	-1248(6)	48(7)
C(12)	1524(29)	3820(20)	-1476(6)	62(8)
C(13)	2520(31)	3758(25)	-1860(8)	81(10)
C(14)	3584(28)	4899(26)	-1853(7)	69(9)
C(15)	3323(29)	5671(22)	-1487(7)	64(9)
C(16)	-182(41)	7315(21)	-1953(8)	96(12)
C(17)	-1549(33)	6232(33)	-1850(9)	93(13)
C(18)	-1417(43)	5412(30)	-2188(10)	108(14)
C(19)	-14(50)	5755(29)	-2473(9)	109(14)
C(20)	649(39)	6916(25)	-2329(8)	101(13)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3

SELECTED BOND DISTANCES AND ANGLES FOR $C_{20}H_{18}Fe_3Br_4$

<i>(a) Bond distances (Å)</i>			
Fe(1)–C(1)	2.062(18)	Fe(1)–C(2)	2.032(23)
Fe(1)–C(3)	2.071(21)	Fe(1)–C(4)	2.064(20)
Fe(1)–C(5)	2.052(18)	Fe(1)–C(6)	2.040(24)
Fe(1)–C(7)	2.014(21)	Fe(1)–C(8)	2.029(23)
Fe(1)–C(9)	2.065(24)	Fe(1)–C(10)	2.006(21)
Fe(2)–C(11)	2.117(21)	Fe(2)–C(12)	2.108(24)
Fe(2)–C(13)	2.034(27)	Fe(2)–C(14)	2.007(23)
Fe(2)–C(15)	2.110(21)	Fe(2)–C(16)	2.055(24)
Fe(2)–C(17)	2.047(25)	Fe(2)–C(18)	2.120(35)
Fe(2)–C(19)	2.061(31)	Fe(2)–C(20)	2.062(27)
Fe(3)–Br(1)	2.339(5)	Fe(3)–Br(2)	2.333(4)
Fe(3)–Br(3)	2.352(4)	Fe(3)–Br(4)	2.327(4)
C(1)–C(2)	1.405(28)	C(1)–C(5)	1.454(25)
C(1)–C(11)	1.451(27)	C(2)–C(3)	1.423(33)
C(3)–C(4)	1.470(30)	C(4)–C(5)	1.381(29)
C(6)–C(7)	1.408(36)	C(6)–C(10)	1.396(33)
C(7)–C(8)	1.411(35)	C(8)–C(9)	1.404(31)
C(9)–C(10)	1.483(33)	C(11)–C(12)	1.412(31)
C(11)–C(15)	1.460(29)	C(12)–C(13)	1.422(38)
C(13)–C(14)	1.397(38)	C(14)–C(15)	1.417(31)
C(16)–C(17)	1.511(37)	C(16)–C(20)	1.373(39)
C(17)–C(18)	1.354(44)	C(18)–C(19)	1.431(52)
C(19)–C(20)	1.317(44)	Fe(3)–Br(1)	2.340(4)
Fe(1)–CNT(1) ^a	1.66(2)	Fe(3)–Br(2)	2.333(4)
Fe(1)–CNT(2)	1.64(2)	Fe(3)–Br(3)	2.351(4)
Fe(2)–CNT(3)	1.69(2)	Fe(3)–Br(4)	2.330(4)
Fe(2)–CNT(4)	1.69(2)		
<i>(b) Bond angles (deg)</i>			
CNT(1)–Fe(1)–CNT(2)	179.5(5)	Br(1)–Fe(3)–Br(4)	108.5(2)
CNT(3)–Fe(2)–CNT(4)	175.8(5)	Br(2)–Fe(3)–Br(3)	109.2(2)
Br(1)–Fe(3)–Br(2)	108.8(2)	Br(2)–Fe(3)–Br(4)	107.7(2)
Br(1)–Fe(3)–Br(3)	111.7(2)	Br(3)–Fe(3)–Br(4)	110.7(2)

^a CNT(1) = centroid (C(1) to C(5)), CNT(2) = centroid (C(6) to C(10)), CNT(3) = centroid (C(11) to C(15)), CNT(4) = centroid (C(16) to C(20)).

TABLE 4

LEAST-SQUARES PLANES FOR BIFERROCENIUM TETRABROMOFERRATE^a

Plane I (C(1) to C(5)):	$0.7663 x - 0.5311 y + 0.3616 z + 3.1223 = 0$
Plane II (C(6) to C(10)):	$0.7624 x - 0.5454 y + 0.3482 z - 0.1339 = 0$
Plane III (C(11) to C(15)):	$0.7115 x - 0.5135 y + 0.4797 z + 3.3826 = 0$
Plane IV (C(16) to C(20)):	$0.6731 x - 0.5247 y + 0.5211 z + 7.0954 = 0$

Dihedral angles between planes (deg)

	II	III	IV
I	1.1	7.5	10.6
II	–	8.3	11.2
III	–	–	3.3

^a All atoms within each plane showed no deviation from planarity within esds (± 0.02 Å).

and fixed in idealized positions ($d(\text{C-H})$ 0.96 Å, thermal parameters equal 1.2 times the isotropic equivalent for the carbon atom to which it was attached). A multiplicative factor for $\Delta f''$ refined to 1.1(1) indicating that the reported enantiomorph is the correct one. The final difference Fourier synthesis showed only a diffuse background (maximum 1.16 e/Å³ located 1.21 Å from Br(1) followed by nine peaks in the 1.1–0.9 e/Å³ range). An inspection of F_0 vs. F_c values and trends based upon $\sin \theta$, Miller index or parity group failed to reveal any systematic error. All computer programs used in the data collection and refinement are contained in the Nicolet program packages P3, SHELXTL (version 3.0) and XP.

Atomic coordinates are provided in Table 2, and selected bond distances and angles in Table 3. Least squares planes for the C₅ rings appear in Table 4.

Results and discussion

The structure of the biferrocenium cation of **1** is shown in Fig. 1. As has been observed in all other structures containing this cation, the Fe atoms adopt a *trans* relationship to the fulvenide ligand to avoid impossibly short C₅H₅...C₅H₅ contacts [1–3]. The rings associated with the ferrocenyl units are staggered (Fig. 2); those associated with Fe(1) are nearly eclipsed with an average staggering angle of 6.5(3)° (cf., 36° for perfect staggering) whereas those of Fe(2) are more staggered, average angle 23.5(3)°. The whole range of stagger angles, from 0 to 36° have been observed for both neutral and cationic ferrocenyl groups. Although there appears to be a tendency for neutral uncrowded ferrocenes to be either nearly or perfectly staggered in the solid state, and for ferrocenium ions to be eclipsed, the frequency of exceptions makes the use of this parameter as an indicator of oxidation state

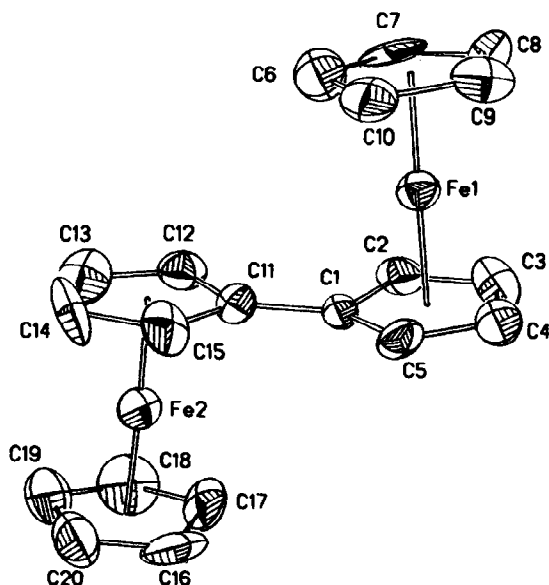


Fig. 1. Molecular structure and labeling scheme for the biferrocenium cation. Hydrogen atoms deleted for clarity and thermal ellipsoids at 50% level.

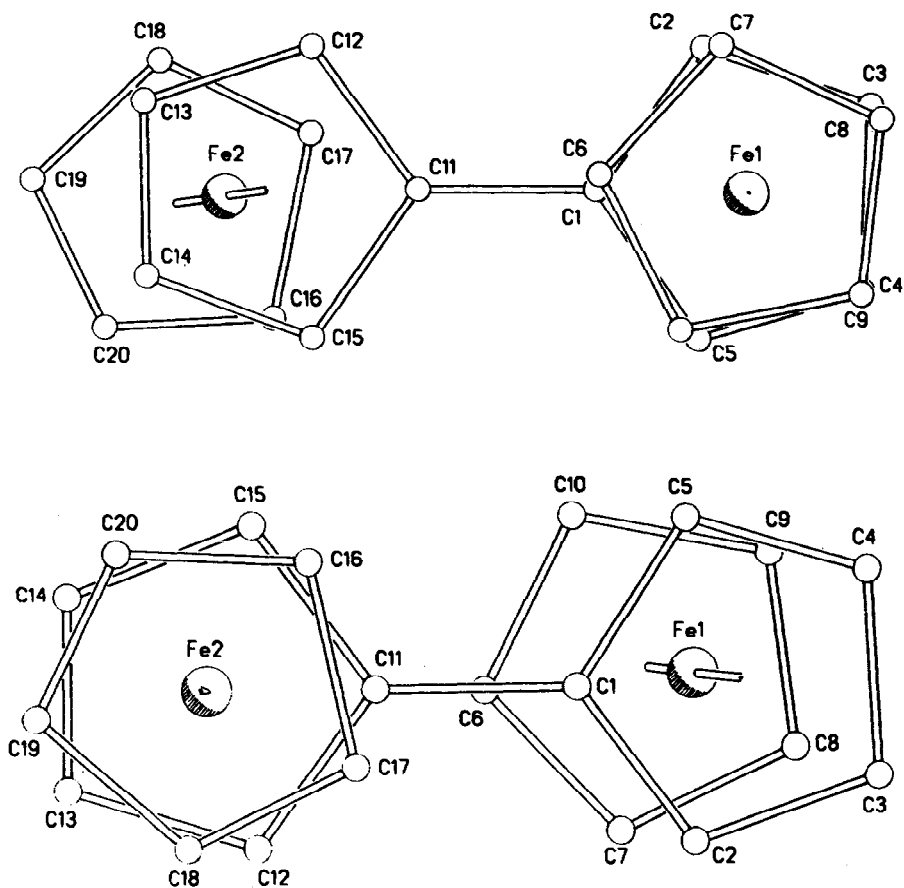


Fig. 2. Structural views revealing the different staggering angles at Fe(1) and Fe(2) as drawn without perspective.

unreliable. Barriers to ring rotation are low and the solid-state ring–ring rotational configurations are likely dominated by packing effects. Neutral biferrocene is staggered 17° , and **2**, biferrocenium triiodide, is perfectly eclipsed [4].

The rings of each ferrocenyl unit are nearly parallel; at Fe(1), the dihedral angle is $1.1(5)^\circ$, at Fe(2), $3.3(5)^\circ$. Between ferrocenyl units, the angle is $7.5(5)^\circ$, whereas this angle is nearly zero in **2**, $0.3(3)^\circ$ [2]. In **2**, the average Fe–C distance is $2.06(1)$ Å, a value midway between those observed for ferrocene (2.045 Å) [5] and the ferrocenium cation (2.075 Å) [4,6–8]. In neutral biferrocene, the average Fe–C distance is $2.03(2)$ Å [9]. In the present study, the average Fe–C distances are marginally different at the two Fe centers: Fe(1), $2.02(2)$ Å; Fe(2), $2.08(2)$ Å. These results suggest a valence-localized description for **1**. The centroid-to-centroid distance ($3.30(2)$ Å) at Fe(1) is significantly shorter than that found at Fe(2) ($3.38(2)$ Å). The centroid-to-centroid distances are, within the quoted esd's, identical to those found in the mixed-valence compound *exo,exo*-1,12-dimethyl[1.1]ferrocenophanium triiodide [10], and indicate that Fe(1) is the Fe^{II} state, and Fe(2), in the Fe^{III} state.

A stereo packing diagram is shown in Fig. 3. If the cation structure contains trapped valences, the cation–anion packing in the crystal lattice should show a

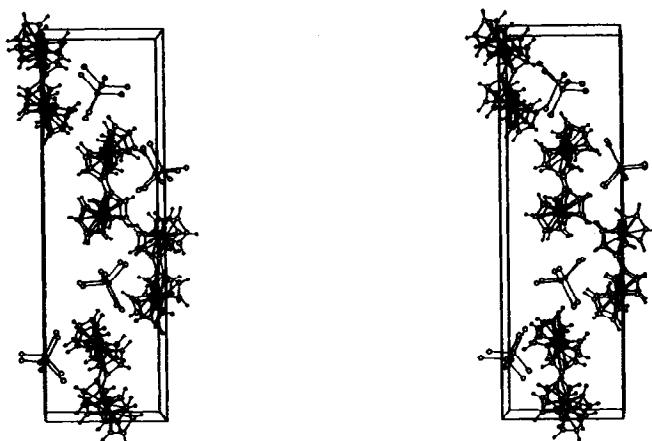


Fig. 3. Stereoview of the unit-cell packing viewed down the a axis.

closer association of the anion with the higher charge of the Fe^{III} "ferrocenium" site, i.e., $\text{Fe}(2)$. For the regular tetrahedral structure of FeBr_4^- (see below) it is assumed that negative charge is equally distributed among the Br atoms. Two interionic contact distances, $\text{Br} \cdots \text{C}$ and $\text{Br} \cdots \text{Fe}(1 \text{ or } 2)$, have been chosen to serve as indicators of the relative closeness of ion approach. In the range 3.60 to 4.00 Å, there are eleven $\text{Br} \cdots \text{C}$ contacts to the rings of $\text{Fe}(2)$ (av. 3.80 Å) and only three to the rings of $\text{Fe}(1)$ (av. 3.88 Å); similarly, in the 4.50–5.00 Å range of $\text{Br} \cdots \text{Fe}(1 \text{ or } 2)$ contacts, three are made to $\text{Fe}(2)$, and one to $\text{Fe}(1)$. This asymmetric placement of the anion relative to the mixed-valence cation is similar to that seen in *exo,exo*-1,12-dimethyl[1.1]ferrocenophanium triiodide [10]. The cations in **1** are packed in pairs with facing coparallel C_5H_5 rings. In **2** a similar stacking is found except that it is continued endlessly in a step-like pattern [2]. In neutral biferrocene, the molecules are more nested and overlapped with rings both top and bottom as found in stacked chairs [9].

The FeBr_4^- anion has an average Fe–Br distance of 2.338(4) Å and an average Br–Fe–Br angle of 109.4(2)°; both values are experimentally identical to those reported for $(\text{H}_3\text{CNH}_3)_2[\text{FeBr}_4]\text{Br}$ [11].

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