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Structure of Decamethylferrocenium Tribromide

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Abstract. $[\mathrm{Fe}\{\mathrm{C_5(CH_3)_5}\}_2]\mathrm{Br_3}$, $M_r = 565{\cdot}8$, orthorhombic, *Cmcm*, $a = 15{\cdot}162\,(5)$, $b = 12{\cdot}358\,(5)$, $c = 11{\cdot}936\,(5)$ Å, $V = 2236{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}681$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 5{\cdot}985$ mm^{-1}, $F(000) = 1124$, room temperature, final $R = 0{\cdot}040$, $wR = 0{\cdot}044$ for 856 reflections with $I \geq 2\sigma(I)$ and 86 variables. The solid is comprised of layers of alternating cations and anions, no significant interactions between the layers are observed.

Introduction. Although a large number of ferrocene derivatives have been characterized by X-ray studies, only comparatively few compounds containing the ferrocenium ion have been investigated. Among these are ferrocenium triiodide (Bernstein & Herbstein, 1968), ferrocenium tetrachloroferrate (Paulus & Schäfer, 1978), 1,1′-dimethylferrocenium triiodide (Bats, de Boer & Bright, 1971) and a series of charge-transfer complexes containing the decamethylferrocenium ion and spacious anions such as tetracyanoethenide (TCNE) and pentacyanopropenide (PCNP), which interact with the ferrocenium moieties and give rise to interesting physical properties, for example, metamagnetism (Miller, Calabrese, Rommelmann, Chittipeddi, Zhang, Reiff & Epstein, 1987, and literature cited therein). Whereas the unsubstituted ferrocenium cations are mostly disordered, so that exact structural information on the cations cannot be obtained, substituted (*e.g.* decamethylferrocenium) cations do not seem to exhibit disorder. With this in view we have determined the crystal structure of the decamethylferrocenium cation with a simple counterion, the $\mathrm{Br_3^-}$ anion.

Experimental. The title compound was prepared by reaction of decamethylferrocene with $\mathrm{Br_2}$ in $\mathrm{CCl_4}$ and recrystallized from methanol. Dark-green crystal plates, dimensions of crystal used for measurement $0{\cdot}5 \times 0{\cdot}2 \times 0{\cdot}05$ mm. Enraf–Nonius CAD-4 diffractometer, graphite-crystal monochromator, Mo $K\alpha$ radiation, unit-cell parameters determined from the angular settings of 25 reflections with $0{\cdot}0 \leq \theta \leq 15°$. Intensity data for 1033 unique reflections up to $\theta = 25°$ in the range $0 \leq h \leq 18$, $0 \leq k \leq 14$, $0 \leq l \leq 14$ measured, using the ω–2θ-scan technique with a scan angle of 1·00° and a variable scan rate with a maximum scan time of 60 s per reflection. Three check reflections measured at intervals of 200 reflections showed no significant intensity variation during the period of measurement. The data set was corrected for Lorentz and polarization effects, a Gaussian absorption correction procedure (Frenz, 1981) was used ($T_{\min} = 0{\cdot}55$, $T_{\max} = 0{\cdot}98$). Systematic absences (hkl with $h + k = 2n + 1$; $h0l$ with h and $l = 2n + 1$; $hk0$ with $h + k = 2n + 1$) suggested space groups *Cmcm*, *Cmc*2$_1$ or *C*2*cm*. The centrosymmetric space group was indicated by intensity statistics and confirmed by the successful structure solution. 856 reflections with $I \geq 2\sigma(I)$ were used for the structure determination. The structure was solved by the heavy-atom method (*SHELXS*86; Sheldrick, 1986); light atoms including H atoms were located by subsequent difference Fourier syntheses. Least-squares refinement on F with *SHELX*76 (Sheldrick, 1976), non-H atoms refined anisotropically; H-atom positions were fixed but their isotropic temperature factors were refined at $U = 0{\cdot}08$ Å^2. Final agreement factors were $R = 0{\cdot}040$ and $wR = 0{\cdot}044$, $w = 0{\cdot}8187/[\sigma(F) + 0{\cdot}0026F^2]$, $S = 1{\cdot}94$, $(\Delta/\sigma)_{\max} = 0{\cdot}1$ for the positional parameters of the non-H atoms, except for those of the methyl-C atom C(6) situated on a mirror plane, for which $(\Delta/\sigma)_{\max} = 0{\cdot}7$, max. and min. residual electron densities 0·22 and $-0{\cdot}27$ e Å^{-3} near the Br atoms. Scattering factors for neutral atoms including anomalous contributions as in *SHELX*76, except for Fe, for which the values were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). Geometric data calculations were performed with *PLATON* (Spek, 1982).

Discussion. Final positional and thermal parameters are given in Table 1, bond distances and angles in Table 2.* Fig. 1 shows an *ORTEP* (Johnson, 1976)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52197 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and* B_{eq} (Å^2) *values*

$$B_{\rm eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Br(1)	0·16684 (5)	0·19833 (6)	0·25	5·62
Br(2)	0·00	0·19744 (7)	0·25	4·37
Fe	0·00	0·72872 (9)	0·25	2·78
C(1)	0·1132 (3)	0·8074 (3)	0·1901 (4)	3·85
C(2)	0·1135 (3)	0·6987 (3)	0·1539 (4)	4·11
C(3)	0·1124 (4)	0·6317 (5)	0·25	4·05
C(4)	0·1184 (4)	0·9040 (5)	0·1161 (6)	5·83
C(5)	0·1194 (6)	0·6612 (6)	0·0348 (5)	6·42
C(6)	0·1200 (8)	0·5115 (7)	0·25	6·12

Table 2. *Bond distances* (Å) *and bond angles* (°)

Br(1)—Br(2)	2·530 (1)	Fe—C(1)	2·098 (4)
Br(1)···Fe	5·065 (1)	Fe—C(2)	2·101 (5)
Br(1)···C(1)	3·668 (5)	Fe—C(3)	2·083 (7)
Br(1)···C(2)	3·523 (5)	C(1)—C(1$^{\rm i}$)	1·431 (9)
Br(1)···C(3)	3·447 (8)	C(1)—C(2)	1·412 (6)
Br(1)···C(4)	3·590 (9)	C(1)—C(4)	1·487 (7)
Br(1)···C(5)	3·884 (6)	C(2)—C(3)	1·414 (9)
		C(2)—C(5)	1·498 (8)
		C(3)—C(6)	1·489 (10)
C(1$^{\rm i}$)—C(1)—C(4)	126·4 (5)	C(1)—C(2)—C(5)	125·8 (5)
C(1$^{\rm i}$)—C(1)—C(2)	107·8 (5)	C(3)—C(2)—C(5)	126·1 (5)
C(2)—C(1)—C(4)	125·7 (5)	C(2)—C(3)—C(2$^{\rm i}$)	108·4 (5)
C(1)—C(2)—C(3)	108·0 (5)	C(2)—C(3)—C(6)	125·6 (5)

Symmetry code: (i) x, y, $0·5 - z$.

plot of the ferrocenium cation and Fig. 2 a packing diagram drawn with *PLUTO* (Motherwell & Clegg, 1978).

The Fe atom occupies a special position [4(*c*)], thus the decamethylferrocenium cation posesses the symmetry C_{2v}; it is exactly eclipsed and may be described idealized as D_{5h}, whereas for decamethylferrocene itself a staggered configuration with D_{5d} symmetry was found (Struchkov, Andrianov, Sal'nikova, Lyatifov & Materikova, 1978; Freyberg, Robbins, Raymond & Smart, 1979). One ring atom, C(3), and the methyl C atom, C(6), connected to this atom, also occupy special positions [8(*g*)] in a mirror plane. The mean value for the Fe—C(ring) distance is 2·097 (5) Å. This agrees well with distances of 2·086–2·096 Å found in the decamethylferrocenium charge-transfer complexes with TCNE and PCNP and in complexes with anions such as $[FeCl_4]^-$ and $[FeBr_4]^-$ (Miller, Calabrese, Rommelmann, Chittipeddi, Zhang, Reiff & Epstein, 1987). It is slightly longer than the average Fe—C distance of 2·050 (2) Å in the parent $[Fe\{C_5(CH_3)_5\}_2]$ compound (Freyberg, Robbins, Raymond & Smart, 1979) and of 2·058 (2) Å found in octamethylferrocene, $[Fe\{C_5(CH_3)_4H\}_2]$ (Struchkov, Andrianov, Sal'nikova, Lyatifov & Materikova, 1978). The distance Fe—ring centroid is 1·715 (7) Å, which also agrees well with the values of 1·694–1·712 Å found in the compounds mentioned above; in $[Fe\{C_5(CH_3)_5\}_2]$ it is 1·656 Å. This confirms the fact that removal of an electron from ferrocene expands the iron-to-ring distance by about 0·05 Å (Hillman & Larson, 1985). However, the average C—C ring bond distance, which is 1·417 (7) Å, remains the same as that in $[Fe\{C_5(CH_3)_5\}_2]$, 1·419 (2) Å, and is also in good agreement with that in $[Fe\{C_5(CH_3)_4H\}_2]$, 1·428 (4) Å. The average C(ring)—C(methyl) distance is 1·492 (6) Å, compared with 1·496 (6) Å in $[Fe\{C_5(CH_3)_4H\}_2]$ and 1·502 (3) Å in $[Fe\{C_5(CH_3)_5\}_2]$.

The Br atoms of the tribromide anion also occupy special positions in a mirror plane, the central atom, Br(2) in positions [4(*c*)], the terminal Br(1) atom in positions [8(*g*)]. Therefore the Br_3^- anion is linear. The Br—Br distance is 2·530 (1) Å, which agrees with values of 2·526–2·569 Å found in Br_3^- ions not constrained by symmetry, *e.g.* in tetra(methylthio)tetrathiofulvalene tribromide (Endres, 1986), as well as in Br_3^- ions constrained by symmetry, *e.g.* in 4-methylpyridinium nonabromoantimonate, in which the anion is centrosymmetric and shows a Br—Br distance of 2·561 (4) Å. The average Br—Br distance, reported for centrosymmetric ions in other structures

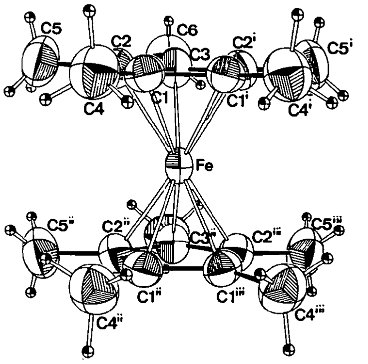

Fig. 1. $[Fe\{C_5(CH_3)_5\}_2]^+$ cation drawn with 50% probability surfaces (H atoms given arbitrary radii). Symmetry code: (i) x, y, $0·5 - z$; (ii) $-x$, y, z; (iii) $-x$, y, $0·5 - z$.

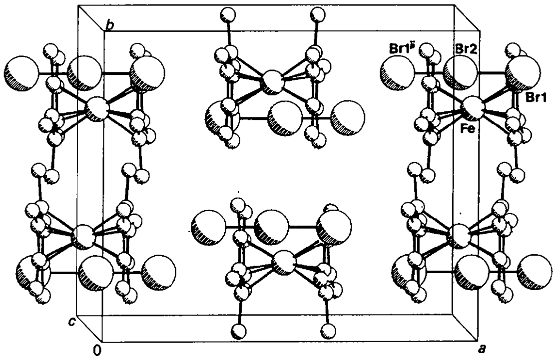

Fig. 2. Packing diagram for $[Fe\{C_5(CH_3)_5\}_2]Br_3$.

(Lawton, Hoh, Johnson & Knisely, 1973, and references cited therein) is 2·54 Å.

The closest distances between the tribromide anion and the decamethylferrocenium cation are 3·447 (8) Å for Br(1)···C(3), and 3·30–3·36 Å for Br(1) and H atoms at the methyl C atoms C(4) and C(5). This rules out stronger bonding interactions between the two moieties.

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Structure of 1,1-Dicarbonyl-1,1-bis(dimethylphenylphosphine)-2,3-bis(methoxycarbonyl)-1-ruthenaindene, a Ruthenium(II) Complex Containing a Five-Membered Metallacycle

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Abstract. $[\overline{Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)C}_6H_4\}(PMe_2Ph)_2]$, $[Ru(C_{12}H_{10}O_4)(C_8H_{11}P)_2(CO)_2]$, M_r = 651·6, triclinic, $P\overline{1}$, a = 11·858 (1), b = 11·958 (1), c = 12·970 (2) Å, α = 99·41 (1), β = 82·42 (1), γ = 60·93 (1)°, V = 1537·4 Å^3, Z = 2, D_x = 1·41 (1) Mg m^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 0·64 mm^{-1}, $F(000)$ = 668, T = 290 (2) K, R = 0·044 for 4556 observed reflections with $F_o > 3\sigma(F_o)$ and 352 parameters. In the solid state the complex exists as discrete monomeric units, with slightly irregular octahedral geometry about the Ru atom. Within the planar five-membered metallacycle the Ru—C dis-