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Structures of (Ferrocenylmethyl)trimethylammonium Iodide and Hexa-*N*-methylferrocene-1,1′-diylbis(methylammonium Iodide)

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Abstract

(Ferrocenylmethyl)trimethylammonium iodide (1), $[C_{14}H_{20}FeN][I]$, M_r = 385.07, monoclinic, $P2_1/c$, a = 8.6236 (5), b = 13.5926 (10), c = 12.8623 (6) Å, β = 102.792 (4)°, V = 1470.3 (2) Å^3, Z = 4, T = 293 K, $F(000)$ = 760, D_x = 1.74 g cm^{-3}, Mo $K\alpha$, λ = 0.71069 Å, μ = 3.08 mm^{-1}, R = 0.024 for 4075 observations [$I > 3\sigma(I)$]. The $[\{(C_5H_5)Fe(C_5H_4)\}\text{-}CH_2N(CH_3)_3]^+$ cation is involved in a three-dimensional network of C—H···I$^-$ interactions (both the cation and anion residing in general positions). The shortest C···I distances are 3.954 (2), 3.992 (2) and 4.009 (3) Å. Hexa-*N*-methylferrocene-1,1′-diylbis(methylammonium iodide) (2), $[C_{18}H_{30}FeN_2].2[I]$, M_r = 584.10, monoclinic, $C2/c$, a = 27.1457 (12), b = 12.3446 (6), c = 14.5295 (10) Å, β = 115.909 (4)°, V = 4379.5 (4) Å^3, Z = 8, T = 293 K, $F(000)$ = 2264, D_x = 1.772 g cm^{-3}, Mo $K\alpha$, λ = 0.71069 Å, μ = 3.48 mm^{-1}, R = 0.031 for 4482 observations [$I > 3\sigma(I)$]. In (2), the $[Fe\{(C_5H_4)CH_2\text{-}N(CH_3)_3\}_2]^{2+}$ cation (which has approximate twofold symmetry) and one of the anions reside in general positions. Another iodide resides on a twofold axis, while a third iodide lies on an inversion centre. A more extensive three-dimensional network of C—H···I$^-$ interactions is present in (2) than in (1) and involves all three of the iodide anions. The shortest C···I$^-$ contacts are 3.733 (4) and 3.848 (4) Å and involve the iodide which resides in a general position (all three iodides have C···I contacts < 4.1 Å).

Introduction

The current interest in structural ferrocene chemistry focuses on a wide variety of derivatives which may have potential applications in (*a*) charge-transfer chemistry (Moore *et al.*, 1993) (*b*) supramolecular chemistry (Beer *et al.*, 1991), (*c*) non-linear optical materials science (Houlton *et al.*, 1993), (*d*) ceramics (Tang *et al.* 1993) and (*e*) molecular inclusion and recognition chemistry (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*,*b*).

Hydrogen bonds often provide the strongest intermolecular forces between molecules in organic molecular crystals and hence often dictate the preferred packing arrangement. The general principles underlying hydrogen-bond formation are reasonably well understood and the structures of hydrogen-bonded crystals can often be rationalized in terms of preferred combinations of hydrogen-bond donors and acceptors (Etter, 1990; Etter, McDonald & Bernstein, 1990; Etter & Reutzel, 1991).

We are currently studying the molecular structures, hydrogen-bonding and molecular-interaction patterns in the crystal lattices of a variety of ferrocene

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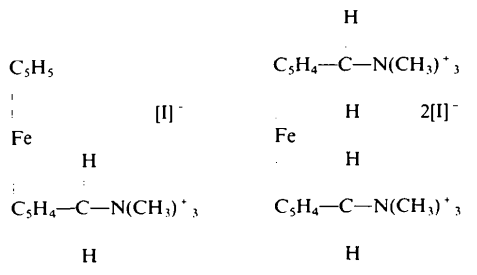
derivatives of the type $Fe[(C_5H_5)(C_5H_4)]CR'R''OH$ or $Fe[(C_5H_4)CR'R''OH]_2$, by changing the substituents at the central C atom. We have noted that the extent and nature of the hydrogen bonding is clearly not a simple function solely of the steric demands about the central C atom (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*). It is anticipated that with the appropriate molecular design within this electroactive ferrocene series, these complexes will have potential application as non-linear optical materials and in molecular inclusion and recognition chemistry.

The salt (ferrocenylmethyl)trimethylammonium iodide, $[(C_5H_5)FeC_5H_4CH_2N(CH_3)_3][I]$ (1), is a valuable synthetic intermediate in ferrocene chemistry as its cation reacts rapidly and efficiently with a wide range of nucleophilic reagents, with displacement of trimethylamine. By contrast, the corresponding 1,1′-disubstituted derivative hexa-*N*-methylferrocene-1,1′-diylbis(methylammonium iodide), $[Fe\{C_5H_4\text{-}CH_2N(CH_3)_3\}_2].2[I]$ (2), reacts more slowly by several orders of magnitude in similar reactions, despite the dipositive charge on the cation. Therefore, we have determined the structures of (1) and (2) in order to assess whether there are any structural or conformational features contributing to the deceleration of substitution reactions in (2). The structure of (1) is also of interest as this compound was the first organometallic structure to be solved *ab initio* from X-ray powder data collected using a conventional laboratory powder diffractometer (Lightfoot, Glidewell & Bruce, 1992), before single crystals were available. The highly accurate structure refinement using single-crystal data reported here for (1) allows comparison with the previous Rietveld refinement, which required the application of soft constraints to most of the interatomic distances in the cation for successful refinement.



(1) (2)

Experimental

Synthesis

Samples of compounds (1) and (2) were prepared from ferrocene by aminomethylation and subsequent methylation (Pauson, Sandhu & Watts, 1966). Single crystals were grown by slow evaporation of solutions in dichloromethane (for 1) or nitromethane (for 2).

Data collection and cell refinement

Enraf-Nonius CAD-4 software was used. The data reduction program used to solve and refine the structure and the software used to prepare the material for publication was *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Details of cell data, data collection and refinement are concisely summarized in Table 1. The space group for (1) was determined unambiguously from the systematic absences (*h*0*l* absent if $l = 2n + 1$, 0*k*0 absent if $k = 2n + 1$) as $P2_1/c$. The systematic absences for (2) (*hkl* absent if $h + k = 2n + 1$, *h*0*l* absent if $l = 2n + 1$) allow the space group to be either $C2/c$ or Cc; the former was assumed and confirmed by the analysis. In both structures, the H atoms attached to the C atoms were clearly visible in difference maps at intermediate stages of refinement. All H atoms were positioned on geometric grounds with only their thermal parameters refined isotropically (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations. There is no solvent of crystallization present in either of the lattices and an examination of the crystal structures using *PLATON* (Spek, 1993*a*) revealed no potential volume for any solvent molecules. The diagrams were prepared using *ORTEP*II (Johnson, 1976) and *PLUTON* (Spek, 1993*b*). Final fractional coordinates* are given in Table 2 and principal dimensions in Table 3.

Results and discussion

The salt (1) crystallizes in the centrosymmetric space group $P2_1/c$ with the cation and iodide anion both residing in general positions in the asymmetric unit, Fig. 1. The cation has approximate mirror symmetry and the Fe—C bond lengths are in the range 2.040 (2)-2.051 (2) Å [mean 2.043 (2) Å] for the unsubstituted cyclopentadienyl ring (C11—C15) and 2.025 (2)-2.050 (2) Å [mean 2.038 (2) Å] for the substituted ring (C21—C25). The Fe···Cp plane distance is 1.650 (1) Å for the unsubstituted cyclopentadienyl ring and 1.638 (1) Å for the substituted cyclopentadienyl ring. These Fe···Cp values are 1.652 (1) Å [1.640 (1) Å] and 1.652 (1) Å [1.645 (1) Å] in the related ferrocenyl(phenyl)methanol molecule (Ferguson, Gallagher, Glidewell & Zakaria, 1993*c*). This seems to indicate that there is a general trend in these unsymmetrical ferrocene derivatives for the mean Fe···Cp distance to be longer in the unsubstituted cyclopentadienyl ring system than the substituted cyclopentadienyl ring. The dihedral angle between the C_5 planes is 2.7 (1)° and they are within 4.6 (1)° of an eclipsed conformation.

* Lists of anisotropic thermal parameters, hydrogen positions, full details of molecular dimensions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71557 (51 pp). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1071]

Table 1. *Summary of crystal data, data collection, solution and refinement details*

Crystal data		
Chemical formula	$[C_{14}H_{20}FeN][I]$	$[C_{18}H_{30}FeN_2].2[I]$
Molecular weight	385.07	584.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	8.6236 (5)	27.1457 (12)
b (Å)	13.5926 (10)	12.3446 (6)
c (Å)	12.8623 (6)	14.5295 (10)
β (°)	102.792 (4)	115.909 (4)
V (Å^3)	1470.26 (15)	4379.5 (4)
Z	4	8
Cation symmetry	None	Approximately twofold
$F(000)$	760	2264
D_x (Mg m^{-3})	1.740	1.772
No. of reflections for cell parameters	25	25
2θ range for cell parameters (°)	39-46	30-54
μ (mm^{-1})	3.08	3.48
Temperature (K)	294	294
Crystal form	Block	Block
Crystal size (mm)	0.35 × 0.45 × 0.75	0.35 × 0.35 × 0.45
Crystal colour	Orange	Orange
Data collection		
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Absorption correction	9 ψ scans	9 ψ scans
T_{min}	0.3666	0.3801
T_{max}	0.5070	0.4629
No. of measured reflections	5360	7840
No. of independent reflections	5081	7589
R_{int}	0.025	0.009
No. of observed reflections	4075	4482
Observation criterion	$I > 3\sigma(I)$	$I > 3\sigma(I)$
$2\theta_{max}$ (°)	64	64
Range of h, k, l	0 → 12	0 → 40
	0 → 20	0 → 18
	-19 → 19	-21 → 21
No. of standard reflections	3 every 40 min	3 every 60 min
Intensity variation (%)	2.0	2.5
Refinement		
Structure solution	Patterson heavy atom	Patterson heavy atom
R	0.024	0.031
wR	0.035	0.043
S	1.47	1.70
No. of parameters used	175	241
No. of reflections used	4075	4482
H-atom treatment	Riding H atoms	Riding H atoms
Weighting	$w = 1/(\sigma^2 F_o + kF_o^2)$	$w = 1/(\sigma^2 F_o + kF_o^2)$
k	0.0003	0.0003
$(\Delta/\sigma)_{max}$	0.011	0.000
$\Delta\rho$ range (e Å^{-3})	-0.78, 0.85	-1.20, 1.17
Extinction correction	Larson (1970)	Larson (1970)
Extinction coefficient	1.146 (046)	0.896 (050)
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)
Computer programs		
System used for all calculations	Silicon Graphics 4D-35TG	Silicon Graphics 4D-35TG
Data collection	*CAD*-4 software	*CAD*-4 software
Cell refinement	*CAD*-4 software	*CAD*-4 software
Data reduction	*NRCVAX DATRD2*	*NRCVAX DATRD2*
Structure solution	*NRCVAX* Patterson map	*NRCVAX* Patterson map
Structure refinement	*NRCVAX LSTSQ*	*NRCVAX LSTSQ*
Molecular graphics	*NRCVAX, ORTEPII, PLUTON*	*NRCVAX, ORTEPII, PLUTON*

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Compound (1)				
I	−0.321554 (20)	0.055175 (12)	0.195671 (12)	0.05155 (8)
Fe	0.16924 (3)	0.175241 (18)	0.463348 (20)	0.02958 (11)
N	−0.26054 (19)	0.35787 (11)	0.34666 (13)	0.0343 (7)
C1	−0.11822 (23)	0.29304 (14)	0.34264 (15)	0.0354 (8)
C2	−0.3529 (3)	0.37102 (19)	0.23459 (19)	0.0502 (11)
C3	−0.3634 (3)	0.30998 (19)	0.41096 (21)	0.0498 (12)
C4	−0.2094 (3)	0.45660 (15)	0.39399 (20)	0.0475 (11)
C11	0.1124 (3)	0.03809 (14)	0.40165 (18)	0.0400 (9)
C12	0.2545 (3)	0.03485 (16)	0.48243 (17)	0.0438 (10)
C13	0.3676 (2)	0.09744 (18)	0.45076 (17)	0.0436 (10)
C14	0.2958 (2)	0.14000 (16)	0.35104 (16)	0.0403 (9)
C15	0.1385 (2)	0.10364 (15)	0.32042 (15)	0.0366 (8)
C21	−0.0122 (3)	0.21447 (14)	0.53124 (16)	0.0387 (8)
C22	0.1338 (3)	0.21896 (18)	0.60810 (16)	0.0481 (11)
C23	0.2351 (3)	0.28660 (17)	0.57166 (18)	0.0483 (10)
C24	0.1529 (3)	0.32512 (14)	0.47233 (17)	0.0396 (9)
C25	−0.0013 (2)	0.28038 (12)	0.44577 (14)	0.0321 (7)
Compound (2)				
I1	0.07826 (1)	0.56034 (2)	0.17568 (2)	0.0607 (2)
I2	0.00000	0.93826 (3)	−0.25000	0.0533 (2)
I3	0.25000	1.25000	0.00000	0.1219 (5)
Fe	0.181826 (17)	0.94386 (3)	0.14909 (3)	0.0370 (2)
C11	0.20549 (14)	0.7859 (3)	0.1646 (3)	0.053 (2)
C12	0.25172 (15)	0.8545 (4)	0.1972 (4)	0.068 (3)
C13	0.24575 (16)	0.9218 (3)	0.1145 (4)	0.065 (3)
C14	0.19612 (15)	0.8954 (3)	0.0300 (3)	0.050 (2)
C15	0.17039 (12)	0.8113 (3)	0.0607 (2)	0.040 (2)
C1*A*	0.11457 (13)	0.7637 (3)	−0.0006 (2)	0.041 (2)
N1*A*	0.11271 (11)	0.6719 (2)	−0.0721 (2)	0.043 (2)
C2*A*	0.12590 (17)	0.7132 (3)	−0.1553 (3)	0.056 (3)
C3*A*	0.15250 (16)	0.5842 (3)	−0.0152 (3)	0.053 (2)
C4*A*	0.05591 (15)	0.6275 (3)	−0.1173 (3)	0.056 (2)
C21	0.18389 (14)	1.1028 (3)	0.1872 (3)	0.053 (2)
C22	0.18887 (20)	1.0368 (4)	0.2698 (3)	0.071 (3)
C23	0.14304 (21)	0.9714 (4)	0.2392 (3)	0.072 (3)
C24	0.10792 (14)	0.9945 (3)	0.1354 (3)	0.051 (2)
C25	0.13324 (12)	1.0758 (2)	0.1023 (2)	0.037 (2)
C1*B*	0.11473 (11)	1.1195 (2)	−0.0027 (2)	0.038 (2)
N1*B*	0.07657 (11)	1.2170 (2)	−0.0267 (2)	0.044 (2)
C2*B*	0.02361 (17)	1.1845 (4)	−0.0284 (4)	0.071 (3)
C3*B*	0.10259 (24)	1.3058 (3)	0.0483 (4)	0.079 (4)
C4*B*	0.06593 (17)	1.2566 (4)	−0.1309 (3)	0.063 (3)

The Csp^3 C1 atom is displaced 0.140 (4) Å from the plane of the substituted C_5 ring towards the Fe atom. There is no evidence for disorder in the unsubstituted cyclopentadienyl ring (C11—C15) from an analysis of the anisotropic thermal parameters. The Csp^3—N and C_{cp}—Csp^3 bond lengths involving C1 are 1.521 (2) and 1.488 (3) Å, respectively. The ranges of C_{cp}—C_{cp} bond lengths are 1.417 (3)-1.428 (3) Å [mean 1.421 (3) Å] and 1.417 (3)-1.437 (3) Å [mean 1.425 (3) Å] for the unsubstituted and substituted cyclopentadienyl rings, respectively.

In the structure of (2), the cation resides in a general position in the space group $C2/c$, one iodide anion resides in a general position, another iodide resides on a twofold axis and a third iodide anion lies on an inversion centre, Fig. 2. The cation has approximate twofold symmetry with both of the substituted cyclopentadienyl systems adopting similar conformations, as evidenced by

Table 3. *Bond lengths and contact distances* (Å)

Compound (1)

Fe—C11	2.043 (2)	N—C4	1.499 (3)
Fe—C12	2.040 (2)	C1—C25	1.488 (3)
Fe—C13	2.048 (2)	C11—C12	1.421 (3)
Fe—C14	2.051 (2)	C11—C15	1.428 (3)
Fe—C15	2.045 (2)	C12—C13	1.421 (3)
Fe—C21	2.025 (2)	C13—C14	1.418 (3)
Fe—C22	2.041 (2)	C14—C15	1.415 (3)
Fe—C23	2.050 (2)	C21—C22	1.420 (3)
Fe—C24	2.047 (2)	C21—C25	1.437 (3)
Fe—C25	2.027 (2)	C22—C23	1.417 (4)
N—C1	1.521 (2)	C23—C24	1.417 (3)
N—C2	1.495 (3)	C24—C25	1.433 (3)
N—C3	1.490 (3)		
I—C1	3.954 (2)	I—C4^{i}	4.173 (3)
I—C15	3.992 (2)	I—C4^{ii}	4.205 (3)
I—C2^{i}	4.009 (3)	I—C12^{iii}	4.232 (2)
I—C3^{ii}	4.039 (3)	I—C24^{iv}	4.237 (2)
I—C11	4.085 (2)		

Compound (2)

Fe—C11	2.034 (3)	C15—C1*A*	1.502 (4)
Fe—C12	2.036 (4)	C1*A*—N1*A*	1.524 (4)
Fe—C13	2.025 (4)	N1*A*—C2*A*	1.493 (4)
Fe—C14	2.022 (3)	N1*A*—C3*A*	1.496 (4)
Fe—C15	2.019 (3)	N1*A*—C4*A*	1.491 (4)
Fe—C21	2.034 (4)	C21—C22	1.408 (6)
Fe—C22	2.034 (4)	C21—C25	1.429 (4)
Fe—C23	2.036 (4)	C22—C23	1.384 (8)
Fe—C24	2.027 (3)	C23—C24	1.417 (6)
Fe—C25	2.018 (3)	C24—C25	1.414 (5)
C11—C12	1.413 (6)	C25—C1*B*	1.483 (4)
C11—C15	1.424 (5)	C1*B*—N1*B*	1.526 (4)
C12—C13	1.410 (7)	N1*B*—C2*B*	1.482 (5)
C13—C14	1.408 (6)	N1*B*—C3*B*	1.488 (5)
C14—C15	1.427 (5)	N1*B*—C4*B*	1.494 (5)
I1—C1*A*	4.005 (3)	I2—C4*A*^{x}	4.264 (4)
I1—C2*A*^{v}	4.041 (4)	I2—C23^{vii}	4.108 (4)
I1—C3*A*	4.090 (4)	I2—C23^{xi}	4.108 (4)
I1—C4*A*	4.113 (4)	I2—C24^{vii}	4.038 (3)
I1—C4*A*^{vi}	4.082 (4)	I2—C24^{xi}	4.038 (3)
I1—C4*A*^{v}	4.049 (4)	I2—C1*B*	4.223 (3)
I1—C2*B*^{vii}	4.120 (4)	I2—C1*B*^{x}	4.223 (3)
I1—C3*B*^{viii}	3.848 (4)	I2—C2*B*	4.268 (6)
I1—C4*B*^{ix}	3.733 (4)	I2—C2*B*^{x}	4.268 (6)
I2—C1*A*	4.195 (3)	I3—C21	4.265 (4)
I2—C1*A*^{x}	4.195 (3)	I3—C21^{xii}	4.265 (4)
I2—C2*A*	4.145 (4)	I3—C1*B*	3.995 (3)
I2—C2*A*^{x}	4.145 (4)	I3—C1*B*^{xii}	3.995 (3)
I2—C4*A*	4.264 (4)		

Symmetry codes: (i) $-1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $-x, -y, 1-z$; (iv) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $x, 1-y, \frac{1}{2}+z$; (vi) $-x, 1-y, -z$; (vii) $-x, 2-y, -z$; (viii) $x, y-1, z$; (ix) $x, 2-y, \frac{1}{2}+z$; (x) $-x, y, -\frac{1}{2}-z$; (xi) $x, 2-y, z-\frac{1}{2}$; (xii) $\frac{1}{2}-x, \frac{5}{2}-y, -z$.

the Fe—C_{cp}—Csp^3—N torsion angles of 173.3 (3) and 177.9 (3)° involving N(1*A*) and N(1*B*), respectively.

The Fe—C bond lengths in (2) are in the range 2.019 (3)-2.036 (4) Å [mean 2.027 (3) Å] for the C11-C15 ring and 2.018 (3)-2.036 (4) Å [mean 2.030 (3) Å] for the C21-C25 ring. The methylene Csp^3—N bond lengths are both 1.526 (4) Å and the Csp^3—C_{cp} bond lengths are 1.502 (4) and 1.483 (4) Å. The mean methyl Csp^3—N bond lengths are 1.493 (4) and 1.488 (5) Å for both trimethylammonium groups. The range and mean of C_{cp}—C_{cp} bond lengths for both rings are 1.408 (6)-1.427 (5) Å [1.416 (6) Å] and 1.384 (8)-1.429 (4) Å [1.410 (6) Å], and these values are similar to those described previously in related structures (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*,*c*). The interplanar angle between the cyclopentadienyl planes is 1.5 (2)° and these rings are within 0.5 (2)° of being eclipsed. The conformation adopted is such that the exocyclic Csp^3 atoms are rotated about a line joining the ring centroids through 72.8 (2)° from an eclipsed conformation. The Csp^3 C1*A* and C1*B* atoms are displaced 0.12 (1) and 0.13 (1) Å from the plane of their respective C_5 rings in the same direction as the Fe atom.

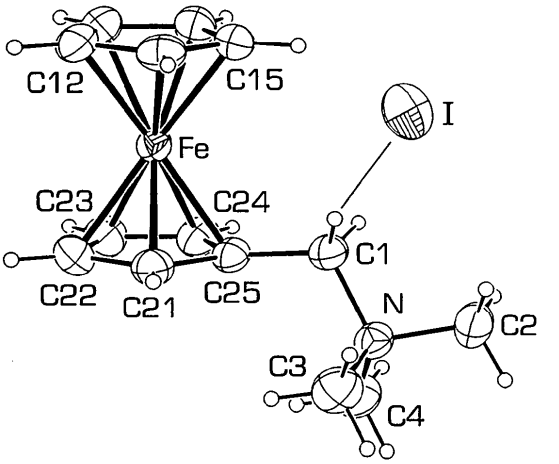


Fig. 1. A view of the asymmetric unit in the (ferrocenylmethyl)-trimethylammonium iodide complex with the non-H atoms shown with thermal ellipsoids drawn at the 50% probability level. For clarity, all H atoms are drawn as small spheres of an arbitrary size.

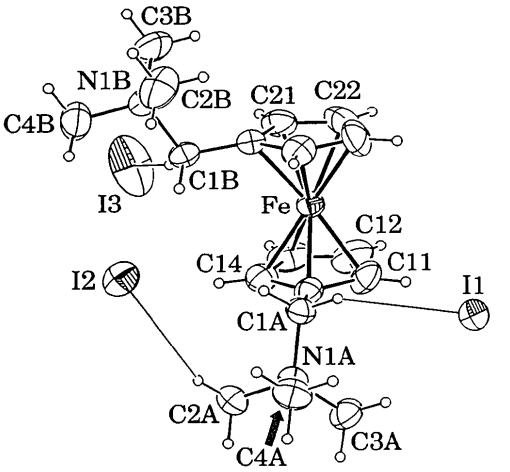


Fig. 2. A view of the asymmetric unit in the hexa-*N*-methylferrocene-1,1′-diylbis(methylammonium iodide) complex. All atoms are shown with thermal ellipsoids and sizes as in Fig. 1.

The inter-ion packing in both (1) and (2) is of interest. In the absence of strong hydrogen-bond (*e.g.* O—H and N—H) donors, there are extensive C—H···I^- interactions in both structures. Well documented cases of C—H···I^- hydrogen bonding are relatively uncommon but where it has been reported (Ferguson, Lough, McAlees & McCrindle, 1993), the C···I^- distance was 3.891 (8) Å. In (1), the unique iodide anion lies in a pocket formed by seven symmetry-related cations with nine C···I^- distances between 3.954 (2) and 4.237 (2) Å, considering all C···I^- contacts < 4.3 Å. A similar situation is found for the three independent iodide anions in (2). The iodide anion which resides in a general position, I1, lies in a pocket formed by six symmetry-related cations with nine C···I^- distances between 3.733 (4) and 4.113 (4) Å. The iodide I2, which resides on the twofold axis, is surrounded by four symmetry-related molecules with 14 (7 × 2) C···I^- interactions between 4.038 (3) and 4.268 (6) Å. The iodide I3, which resides on an inversion centre, is in contact with only two symmetry-related molecules having four (2 × 2) C···I^- contacts of 3.995 (3) and 4.265 (4) Å. The thermal parameters for I3 are markedly larger than those of I1 and I2 because it is not involved in as many C—H···I^- interactions as the other two iodide anions and is held loosely in the pocket in which it resides. If this extensive ion association persists to some degree in solution, it may contribute to the marked reactivity differences observed between (1) and (2).

The structure of the (ferrocenylmethyl)trimethylammonium cation has been reported previously for the salts containing the counterions $B_3H_8^-$ (Fu, Pan, Lu, Zhang & Zhu, 1982) and $B_{10}H_{10}^{2-}$ (Zhang *et al.*, 1982); both cations have the same fully eclipsed conformation found here for (1). The closely related (ferrocenylmethyl)dimethylammonium cation has been structurally characterized both as the tetrachlorozincate (Gibbons & Trotter, 1971) and as the $B_{12}H_{12}^{2-}$ salt (Zhang *et al.*, 1983), while the (ferrocenylmethyl)ethyldimethylammonium cation has been studied as its $B_{20}H_{18}^{2-}$ salt (Siriwardane, Chu, Hosmane, Zhu & Zhang, 1989). In addition, the structure of *N*-(ferrocenylmethyl)pyridinium iodide has been analysed (Brown & Hall, 1977).

The structure of (1) derived earlier from X-ray powder data (Lightfoot, Glidewell & Bruce, 1992), although of much lower precision than the structure for (1) reported here, is acceptably accurate in most respects, except for the geometry about the N atom. The structure of the rigid ferrocene is well determined, apart from the more flexible side chain. The powder data gave C—CH_2 and CH_2—N distances of 1.53 (5) and 1.44 (2) Å, respectively, which are reversed from the values of 1.488 (3) and 1.521 (2) Å reported here. More serious is the range of bond angles around the N atom which are reported here as 107.3 (2)–111.5 (2)°, but where the best refinement of the powder data gave the range 92 (3)–137 (3)°. This comparison enjoins caution in the use of powder data for the refinement of flexible structures which have considerable thermal motion, but confirms its value for more rigid fragments. H atoms were not allowed for in the powder study and the extensive C—H···I^- interactions were not detected.

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