

## The twinned structure of ferricenyltrifluoroborate

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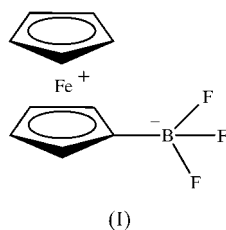
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Crystals of the title compound,  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{BF}_3)]$ , are monoclinic and twinned. The twinning initially resulted in a misleading unit-cell assignment. The formal oxidation state of Fe is 3+, and the crystal packing consists of intermolecular  $\text{C}-\text{H}\cdots\text{F}$  and  $\pi-\pi$  interactions.

### Comment

Oligonuclear aggregates of organometallic compounds are receiving increased attention because of their potential applications as magnetic, electronic and liquid-crystalline materials. We have recently synthesized the trinuclear ferrocene complex 1,3,5-tris(4-methoxyphenyl)-2,4,6-triferrocenylborazine in order to investigate the efficiency of a borazine bridging unit as a transmitter of electronic interactions (Ma *et al.*, 2002). Partial oxidation of that compound was expected to lead to a mixed-valence state with interesting electronic and spectroscopic properties. For this reason, the compound was treated with the oxidizing agent  $\text{AgBF}_4$  in various stoichiometric ratios. In most cases, a small number of dark-colored crystals of (I) were obtained from the reaction mixture. Thus 1,3,5-tris(4-methoxyphenyl)-2,4,6-triferrocenylborazine is not stable in the presence of  $\text{AgBF}_4$ , but decomposes to give ferricenyltrifluoroborate, (I).



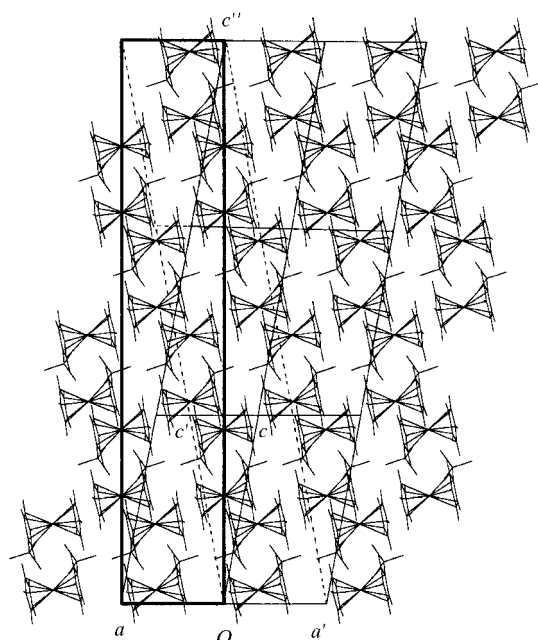
Crystals of (I) were found to be twinned, and the twinned cell can be obtained by the unit-cell transformation  $a_{\text{twin}} = -a$ ,  $b_{\text{twin}} = -b$  and  $c_{\text{twin}} = c + 2a/3$  (see Fig. 1). Initially, the unit-

cell assignment resulted in an orthogonal cell with a volume three times that of the correct monoclinic unit cell and a  $\beta_{\text{ortho}}$  angle of  $90.001$  ( $13^\circ$ ) at 146 K. The assignment of the correct crystal system was only possible after the structure had been determined and refined. This ambiguity could have been avoided if the structure determination had been performed at a higher temperature. Cell measurements at different temperatures gave  $\beta_{\text{ortho}}$  angles of  $90.241$  ( $13^\circ$ ),  $90.111$  ( $11^\circ$ ) and  $90.047$  ( $12^\circ$ ) at 294, 224 and 174 K, respectively. At room temperature, several reflection profiles were split and the twinning of the crystal was quite obvious.

The ferrocene group has an eclipsed conformation (Fig. 2). The  $\text{C}-\text{Cg}1-\text{Cg}2-\text{C}$  torsion angles range from  $3.6$  to  $4.1^\circ$  for the five eclipsed atom pairs ( $\text{Cg}1$  and  $\text{Cg}2$  are the centroids of the two five-membered rings), and the angle between the two cyclopentadiene planes is  $1.64$  ( $8^\circ$ ). The B atom deviates by  $0.027$  ( $5$ ) Å from the  $\text{C}11-\text{C}15$  plane and is slightly tilted toward the center of the molecule. The  $\text{Fe}-\text{C}11$  bond length (involving the  $\text{BF}_3$ -substituted C atom) is about  $0.02$  Å longer than the other nine  $\text{Fe}-\text{C}$  bond lengths. The ring bond angle at atom  $\text{C}11$  [ $105.8$  ( $2^\circ$ )] is  $\sim 2^\circ$  smaller than the value in unsubstituted ferrocene ( $108.0^\circ$ ; Seiler & Dunitz, 1979, 1982). The average  $\text{Fe}-\text{C}$  bond length in (I) [ $2.084$  ( $3$ ) Å] is comparable to  $\text{Fe}-\text{C}$  bond lengths in ferrocenium cations but is about  $0.04-0.05$  Å longer than  $\text{Fe}-\text{C}$  bond lengths in neutral ferrocene groups. As  $\text{Fe}-\text{C}$  bonds in several ferrocenyl and ferrocene groups are considerably affected by libration, however, it appears more realistic to consider the distances from the Fe atom to the centers of the cyclopentadiene rings as a measure of the formal oxidation state of the Fe atom. Values of  $1.697$  ( $2$ ) and  $1.703$  ( $2$ ) Å are observed in (I), which are in very good agreement with the range  $1.686-1.702$  Å (mean  $1.696$  Å) found for a number of ferrocenium cations (Sullivan & Foxman, 1983; Rheingold *et al.*, 1983; Bullen *et al.*, 1986; Cotton *et al.*, 1998), thus confirming the formal oxidation state of Fe in (I) as 3+. The distances of the  $\text{Fe}^{2+}$  ions from the centers of the cyclopentadiene rings in the crystal structure of ferrocene are between  $1.646$  and  $1.661$  Å, with a mean value of  $1.653$  Å (Seiler & Dunitz, 1979, 1982). A mean value of  $1.646$  Å was found in a recent determination of a ferrocenyltrifluoroborate anion (Quach *et al.*, 2001a), in which Fe has a formal oxidation state of 2+. Otherwise, the dimensions of the neutral molecule and the anion are similar. The  $\text{B}-\text{C}$  bond distance is little affected by the charge of the ferrocene group. The value of  $1.616$  ( $4$ ) Å in (I) agrees within experimental uncertainty with the values of  $1.605$  ( $4$ ) and  $1.608$  ( $3$ ) Å found for the anion and is also similar to the values of  $1.600$  ( $3$ ) and  $1.610$  ( $10$ ) Å found in phenyltrifluoroborate anions (Conole *et al.*, 1995; Quach *et al.*, 2001b). Longer  $\text{B}-\text{C}$  distances of  $1.63$ ,  $1.64$ ,  $1.65$  and  $1.66$  Å have, however, been observed in ferricenyltriferrocenylborate (Cowan *et al.*, 1979). Thus, the difference in electronegativity between fluorine and ferrocene has a measurable influence on the  $\text{B}-\text{C}$  bond length.

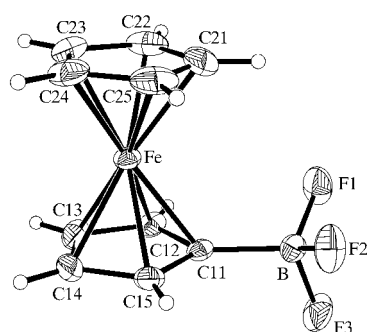
There are no short intramolecular contacts, but the crystal packing exhibits four intermolecular  $\text{C}-\text{H}\cdots\text{F}$  interactions, with  $\text{H}\cdots\text{F}$  distances of less than  $2.6$  Å (Fig. 3 and Table 1). One  $\text{C}-\text{H}\cdots\text{F}$  interaction ( $\text{C}13-\text{H}13\cdots\text{F}2$ ) is very short and

has an H...F distance of only 2.24 Å. The other three C—H...F interactions have H...F distances of 2.43, 2.53 and 2.58 Å. Neighboring ferrocenyl groups translated in the *a*



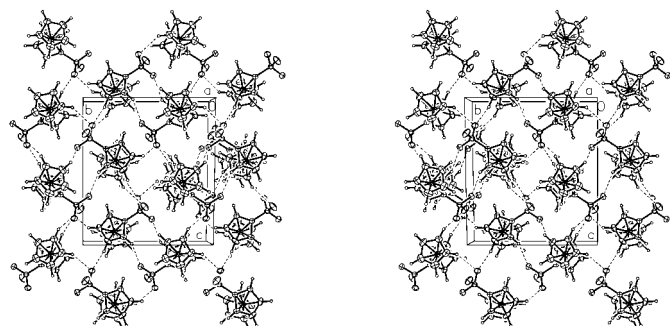
**Figure 1**

A projection of the structure of (I) along *b*. The monoclinic lattice defined by *a* and *c* is represented by solid lines, the twin lattice defined by *a'* and *c'* is represented by broken lines, and the pseudo-orthogonal lattice defined by *a* and *c'* is indicated by bold lines.



**Figure 2**

The molecular structure of (I), with displacement ellipsoids shown at the 50% probability level.



**Figure 3**

The crystal packing of (I), viewed along *a*.

direction are connected by  $\pi$ - $\pi$  interactions between the cyclopentadiene rings. The shortest contact is 3.251 (4) Å, between atom C13 and atom C24 at (*x* - 1, *y*, *z*).

## Experimental

A dry solution of AgBF<sub>4</sub> (25 mg, 0.139 mmol) in tetrahydrofuran (THF, 2.0 ml) was added dropwise at room temperature, with stirring, to a solution of 1,3,5-tris(4-methoxyphenyl)-2,4,6-triferrocenylborazine (40 mg, 0.042 mmol) in THF (~3.0 ml). The color of the solution changed gradually from yellow to blue and the resulting mixture was stirred at room temperature for ~2 h. After all insolubles had been removed by filtration, the filtrate was evaporated *in vacuo* to yield a deep-blue solid and the crude product was dissolved in dry acetonitrile (~10 ml). Deep-blue, almost black, crystals of (I) were obtained by gas-phase diffusion (at room temperature) of dry diethyl ether into the acetonitrile solution of (I) over a period of one month.

## Crystal data

[Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>4</sub>BF<sub>3</sub>)]  
*M<sub>r</sub>* = 252.83  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 6.8603 (10) Å  
*b* = 11.248 (2) Å  
*c* = 12.804 (3) Å  
 $\beta$  = 100.290 (13)°  
*V* = 972.1 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.728 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 118 reflections  
 $\theta$  = 3–23°  
 $\mu$  = 1.55 mm<sup>-1</sup>  
*T* = 146 (2) K  
 Rod, deep blue  
 0.45 × 0.12 × 0.08 mm

## Data collection

Siemens SMART 1K CCD diffractometer  
 $\omega$  scans  
 Absorption correction: numerical (SHELXTL; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.596, *T<sub>max</sub>* = 0.886  
 20 212 measured reflections  
 5254 independent reflections  
 4283 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.046  
 $\theta_{\max}$  = 32.0°  
*h* = -9 → 10  
*k* = -16 → 16  
*l* = -18 → 18  
 385 standard reflections  
 frequency: 600 min  
 intensity decay: none

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.066  
*wR*(*F*<sup>2</sup>) = 0.127  
*S* = 1.30  
 5254 reflections  
 137 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.58 \text{ e } \text{Å}^{-3}$

**Table 1**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C12—H12...F1 <sup>i</sup>	0.95	2.43	3.168 (3)	135
C13—H13...F2 <sup>ii</sup>	0.95	2.24	3.138 (3)	158
C23—H23...F3 <sup>iii</sup>	0.95	2.58	3.455 (4)	154
C24—H24...F2 <sup>iv</sup>	0.95	2.53	3.232 (4)	130

Symmetry codes: (i)  $-x, -y, 1 - z$ ; (ii)  $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iv)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ .

The initial unit-cell determination of (I) revealed an orthogonal cell [*a* = 6.8615 (7) Å, *b* = 11.2481 (16) Å, *c* = 37.781 (6) Å,  $\alpha = \beta = \gamma = 90^\circ$  and *V* = 2915.9 (9) Å<sup>3</sup>]. Merging of the equivalent reflections showed the crystal system to be monoclinic (*R<sub>int</sub>* = 0.054) rather than

orthorhombic ( $R_{\text{int}} = 0.211$ ), and the systematic absences indicated the monoclinic space group  $P2_1/c$ . No acceptable orthorhombic space group could be found. Initially, the structure was determined and refined assuming the space group to be  $P2_1/c$ . Each reflection,  $hkl$ , coincided with a twin reflection,  $h\bar{k}l$ , and the twin fraction refined to 0.369 (1). Refinement in  $P2_1/c$  converged at  $wR2 = 0.167$  and  $R1 = 0.099$ , and the resulting structure contained three independent molecules that were found to be related by translation vectors of  $\frac{2}{3}0\frac{1}{3}$  and  $\frac{1}{3}0\frac{2}{3}$ . Thus, the pseudo-orthogonal cell is an artifact of the twinning and the correct unit cell has a volume of one-third of the observed cell. The new monoclinic unit cell can be obtained from the pseudo-orthogonal cell by the transformation  $a_{\text{new}} = a_{\text{ortho}}$ ,  $b_{\text{new}} = b_{\text{ortho}}$  and  $c_{\text{new}} = -a_{\text{ortho}}/3 + c_{\text{ortho}}/3$ , while the unit cell of the twin domain is obtained by the transformation  $a_{\text{twin}} = -a_{\text{ortho}}$ ,  $b_{\text{twin}} = -b_{\text{ortho}}$  and  $c_{\text{twin}} = a_{\text{ortho}}/3 + c_{\text{ortho}}/3$ . Reflections  $hkl$  of the main domain coincide with reflections  $\bar{h}, \bar{k}, l + 2h/3$  of the twin domain for  $h = 3n$ , while no overlap occurs for reflections with  $h = 3n + 1$  or  $3n + 2$ . Reflections with  $h = 3n$  were omitted from the final cell refinement so that lattice constants unbiased by twinning could be obtained. The space group of the new cell is  $P2_1/n$ . H atoms were positioned geometrically and were refined using a riding model, with fixed individual displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ] and a fixed H—C distance of 0.95 Å. Reflections of both the major domain and the twin domain were used for the structure refinement. The final value of the twin fraction refined to 0.371 (1).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1265). Services for accessing these data are described at the back of the journal.

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