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Crystal Structure Communications

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Intermolecular O—H···O and C—H···π(C$_5$H$_5$), and intramolecular C—H···O interactions in 2-(ferrocenyl)thiophene-3-carboxylic acid

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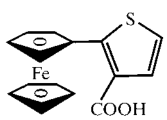
The title compound, [Fe(C$_5$H$_5$)(C$_{10}$H$_7$O$_2$S)], an important precursor *en route* to organometallic donor–π–acceptor systems, forms dimers in the solid state through cyclic intermolecular carboxylic acid O—H···O hydrogen bonds, graph set $R_2^2(8)$ [O···O 2.661 (2) Å and O—H···O 175°]. Intermolecular C$_{\rm Cp}$—H···$\pi_{\rm Cp}$ interactions between the unsubstituted cyclopentadienyl (Cp) rings and C$_{\rm thiazole}$—H···$\pi_{\rm Cp}$ interactions link neighbouring molecules into a three-dimensional network [C···*Cg* 3.753 (7) Å and C—H···*Cg* 156°, and C···*Cg* 3.687 (3) Å and C—H···*Cg* 129°; *Cg* is the ring centroid]. Intramolecular C—H···O interactions are present, graph set *S*(7) [C···O 2.925 (3) Å and C—H···O 120°, and the closest C—H···S$_{\rm thienyl}$ contact has a C···S distance of 3.058 (2) Å].

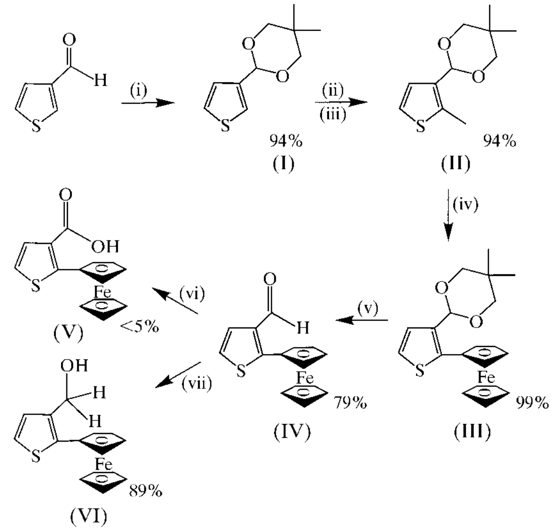
Comment

The design of new redox-active compounds for application in materials science has engaged chemists in recent years. Ferrocene derivatives which are efficient redox systems have been studied extensively as charge-transfer complexes, in molecular recognition science, in peptide chemistry and as non-linear optical materials (Moore *et al.*, 1993; Chesney *et al.*, 1998; Glidewell *et al.*, 1997; Kraatz *et al.*, 1999; Hudson *et al.*,



(V)

2001). An understanding of the interactions present in the crystal structure of a new material can provide valuable information on the hydrogen-bonding modes, thus facilitating an understanding of solid-state effects and the subsequent design and improvement of currently available systems. The structure of 2-(ferrocenyl)thiophene-3-carboxylic acid, (V), an important precursor *en route* to organometallic donor–π–acceptor systems, is reported herein.



Reagents and conditions: (i) neopentyl glycol, catalytic *p*-toluenesulfonic acid, toluene, reflux, 1.5 h; (ii) BuLi, Et$_2$O, 195–293 K; (iii) I$_2$, Et$_2$O, 195–293 K; (iv) ferrocenyllithium, ZnCl$_2$, tetrahydrofuran–hexane (50/50), Pd(PPh$_3$)$_4$, 18 h; (v) oxalic acid, water–tetrahydrofuran (50/50), reflux, 30 min; (vi) 5% KMnO$_4$, ethanol–water (50/50), 12 d, 293 K; (vii) LiAlH$_4$, diethyl ether, room temperature, 12 h.

The synthesis of compound (V) is detailed in the *Experimental* section and the molecular structure is depicted, with the atomic numbering scheme, in Fig. 1; selected geometric dimensions are given in Table 1. Bond lengths are in accord with the anticipated values (Orpen *et al.*, 1994). The unsubstituted cyclopentadienyl (Cp) ring is disordered over two sites, with occupancies of 0.691 (18) and 0.309 (18) for the major and minor orientations, respectively. Rotational disorder is often observed in the unsubstituted C$_5$H$_5$ ring of ferrocene derivatives, *e.g.* 1-ferrocenyl-1-phenylethanol (Ferguson *et al.*, 1993). The Fe1—C bond lengths for the substituted Cp ring of (V) are in the range 2.028 (2)–2.050 (2) Å, which is similar to that observed for the major orientation of the unsubstituted Cp ring [2.039 (4)–2.051 (7) Å]. The Fe1···*Cg*1 and Fe1···*Cg*2 distances are 1.6435 (10) and 1.656 (3) Å, respectively, and the

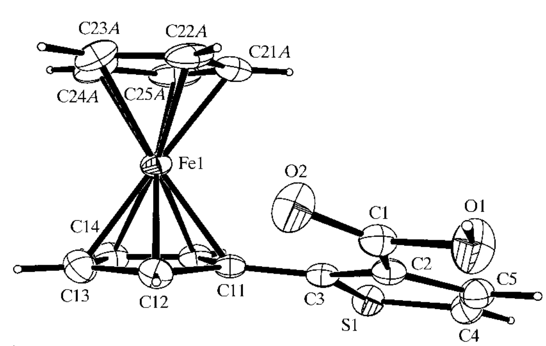


Figure 1
An *ORTEX* (McArdle, 1995) view of (V) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The minor Cp-ring disorder form has been omitted for clarity.

*Cg*1···Fe1···*Cg*2 angle is 178.42 (11)°, where *Cg*1 and *Cg*2 are the centroids of the substituted and unsubstituted Cp rings in the major orientation, *A*. The Cp rings deviate from eclipsed geometry, as indicated by the C1*nA*/*B*···*Cg*1···*Cg*2···C2*nA*/*B* torsion angles, which are in the ranges 20.6 (5) to 21.3 (5)° for *A* (*n* = 1–5) and −5.1 (10) to −16.0 (7)° for the minor orientation, *B*.

There is significant bending of the thienyl group with respect to the substituted Cp ring, with C3 bent away by 0.098 (3) Å from the C11–C15 plane and on the opposite side to Fe1; the C3—C11···*Cg*1 angle is 175.21 (15)°. The thienyl system is oriented at an angle of 20.94 (12)° to the C_5H_4 ring and 5.95 (15)° to the O1/O2/C1/C2 carboxylic acid plane. The angles involving the COOH group are normal (Gallagher *et al.*, 2000). However, the angles centred at C2 are noteworthy. The C1—C2—C3 and C1—C2—C5 angles are 126.48 (18) and 120.82 (18)°, respectively, while the C2—C3—C11 angle is 135.23 (17)°, compared with 115.32 (14)° for S1—C3—C11. Analysis of the C3—C11—C12 and C3—C11—C15 angles, which are 129.38 (17) and 123.97 (18)°, respectively, also suggests that the former C—C—C angles expand considerably due to the combined effects of hydrogen bonding and repulsion about the C3—C11 bond. The angle expansion on the carboxylic acid side of the substituted Cp ring arises where a C—H···O intramolecular interaction is present, graph set *S*(7) [C12···O2 2.925 (3) Å and C12—H12···O2 120°], resulting in a twist by 20.94 (12)° of the thienyl ring from coplanarity with the C_5H_4 group about the C3—C11 bond.

Compound (V) assembles as hydrogen-bonded dimers through cyclic intermolecular carboxylic acid O1—H1···O2^{i} hydrogen bonding, graph set $R_2^2(8)$, in the solid state (Fig. 2) [O1···O2^{i} 2.661 (2) Å and O1—H1···O2^{i} 175°; symmetry code: (i) 1 − *x*, 2 − *y*, 1 − *z*]. Intermolecular C_{Cp}—H···π_{Cp} interactions between the unsubstituted Cp rings link neighbouring molecules into a zigzag chain and, in combination with the dimers, form a two-dimensional network [C25*A*···*Cg*2^{ii} 3.753 (7) Å and C25*A*—H25*A*···*Cg*2^{ii} 156°; symmetry code: (ii) $\frac{1}{2} - x, y - \frac{1}{2}, -z$]. Stacking of the thiophene carboxylic moieties about inversion centres occurs, with an interplanar spacing of 3.46 Å. A $C4_{thiazole}$—H4···*Cg*1^{iii} interaction extends the interactions to form a three-dimensional network [symmetry code: (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z$]. The closest C—H···S contact is C15···S1 3.058 (2) Å, with C15—H15···S1 97° (Table 2).

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for molecules containing the ferrocenyl group directly bonded to a thienyl ring, suggests that such compounds are rare. Current research on chiral ferrocene derivatives implies that (V) may be of interest as a precursor to heterobimetallic systems, as it contains both thienyl and COOH donor groups.

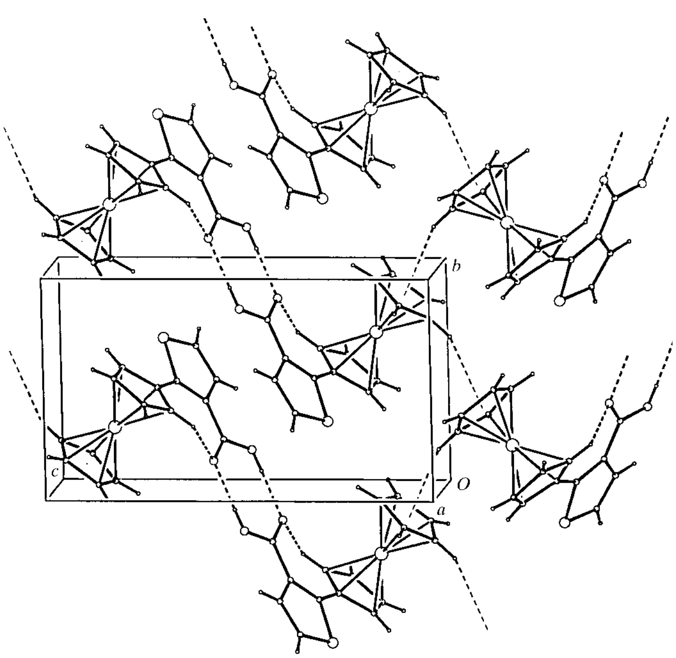


Figure 2
A view of the primary interactions in the crystal structure of (V).

Experimental

Compound (V) was prepared as follows: 3-thiophene carboxaldehyde was protected as its neopentyl acetal, (I), in excellent yield (94%) and *o*-directed metallation with BuLi (Slocum & Gierer, 1976) gave the 2-iodo isomer, (II), exclusively (94%), after quenching with molecular iodine. Pd-catalysed cross coupling with ferrocenyl zinc chloride (Guillaneux & Kagan, 1995; Hudson *et al.*, 2000) afforded the ferrocenyl adduct, (III), in quantitative yield as an orange oil. Deprotection with oxalic acid in a 1:1 mixture of tetrahydrofuran and water at reflux gave the aldehyde, (IV), in good yield (79%) as a red gum. Oxidation of substituents in direct electronic communication with ferrocene is known (Rosenblum, 1965); however, oxidation of (IV) under varying conditions to form (V) resulted either in complete decomposition of the starting material or in no reaction. Compound (V) could only be obtained in very low yield (<5%) by the action of ethanolic potassium permanganate on (IV) for 2 weeks. It is worth noting that the reduction of (IV) was extremely facile and proceeded in high yield (89%) with $LiAlH_4$ in diethyl ether to afford (VI) as an orange crystalline solid. The detailed synthesis of (V) from (IV) is as follows: compound (IV) (0.1 g, 0.34 mmol) was added to a 5% solution of $KMnO_4$ in ethanol/water (50/50; 5 ml) and stirred for 12 d at room temperature. The mixture was extracted with diethyl ether (2 × 50 ml) and the organic portions were combined and washed with water (2 × 50 ml) before being dried over magnesium sulfate and evaporated to dryness. The black residue was purified by column chromatography on silica gel with CH_2Cl_2 as the eluant, to afford (V) as a red solid (0.005 g, <5%). Careful evaporation of a CH_2Cl_2 solution afforded red crystals of (V). Spectroscopic analysis, ^{1}H NMR (270 MHz; δ p.p.m., $CDCl_3$): 7.39 (*d*, 1H, *J* = 5.50 Hz, thiophene), 7.09 (*d*, 1H, *J* = 5.31 Hz, thiophene), 4.82 (*m*, 2H, α-C_5H_4), 4.37 (*m*, 2H, β-C_5H_4), 4.16 (*s*, 5H, C_5H_5).

Crystal data

$[Fe(C_5H_5)(C_{10}H_7O_2S)]$	D_x = 1.635 Mg m^{-3}
M_r = 312.16	Mo *K*α radiation
Monoclinic, $P2_1/a$	Cell parameters from 75 reflections
a = 12.7108 (8) Å	θ = 6.2–20.2°
b = 7.4801 (6) Å	μ = 1.346 mm^{-1}
c = 14.2397 (9) Å	*T* = 294 (1) K
β = 110.542 (5)°	Plate, red
V = 1267.80 (15) Å^3	0.48 × 0.28 × 0.05 mm
Z = 4	

Table 1
Selected geometric parameters (Å, °).

Fe1—C11	2.0488 (19)	O1—C1	1.316 (2)
Fe1—C12	2.050 (2)	O2—C1	1.222 (3)
Fe1—C13	2.045 (2)	C1—C2	1.472 (3)
Fe1—C14	2.032 (2)	C2—C3	1.388 (3)
Fe1—C15	2.028 (2)	C2—C5	1.430 (3)
S1—C3	1.7296 (19)	C3—C11	1.460 (3)
S1—C4	1.712 (2)	C4—C5	1.344 (3)
C3—S1—C4	93.29 (11)	C3—C2—C5	112.63 (18)
O1—C1—O2	122.11 (19)	S1—C3—C2	109.31 (15)
O1—C1—C2	113.14 (18)	S1—C3—C11	115.32 (14)
O2—C1—C2	124.74 (18)	C2—C3—C11	135.23 (17)
C1—C2—C3	126.48 (18)	S1—C4—C5	111.17 (17)
C1—C2—C5	120.82 (18)	C2—C5—C4	113.6 (2)
O1—C1—C2—C5	−5.7 (3)	C2—C3—C11—C12	−19.8 (4)
C1—C2—C3—C11	−8.0 (4)	S1—C3—C11—C15	−18.6 (2)
S1—C3—C11—C12	155.42 (18)	C2—C3—C11—C15	166.2 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the substituted and unsubstituted Cp rings in the major orientation, *A*.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.82	1.84	2.661 (2)	175
C12—H12···O2	0.93	2.34	2.925 (3)	120
C15—H15···S1	0.93	2.80	3.058 (2)	97
C25*A*—H25*A*···*Cg*2^{ii}	0.93	2.88	3.753 (7)	156
C4—H4···*Cg*1^{iii}	0.93	3.03	3.687 (3)	129

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

Data collection

Bruker *P*4 diffractometer	R_{int} = 0.020
ω scans	θ_{max} = 28°
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -16 \rightarrow 1$
	$k = -9 \rightarrow 1$
T_{min} = 0.64, T_{max} = 0.99	$l = -17 \rightarrow 18$
3919 measured reflections	3 standard reflections
3032 independent reflections	every 197 reflections
2431 reflections with $I > 2\sigma(I)$	intensity variation: ±0.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.5075P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	
$wR(F^2) = 0.082$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3032 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
203 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
H-atom parameters constrained	

All H atoms were allowed for as riding atoms with O—H = 0.82 Å and C—H = 0.93 Å using *SHELXL*97 (Sheldrick, 1997) defaults. Disorder in the unsubstituted ring was treated by generating coordinates for the minor component and subsequent use of the *AFIX*59 command in *SHELXL*97 with appropriate *DELU*/*ISOR* controls, to give site occupancies of 0.691 (18) and 0.309 (18) in the final refinement cycles. Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEX* (McArdle, 1995) and *PLATON*; software used to prepare material for publication: *SHELXL*97 and *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1424). Services for accessing these data are described at the back of the journal.

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