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Methyl 2-[(ferrocenylcarbonyl)amino]-thiophene-3-carboxylate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.079
Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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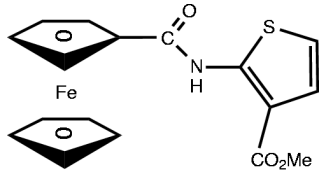
The title compound, $[Fe(C_5H_5)(C_{12}H_{10}NO_3S)]$, was synthesized from ferrocenecarboxylic acid and methyl 2-aminothiophene-3-carboxylate in modest yield. The substituted ring system is essentially planar through the amidothienylcarboxylate moiety, η^5-$(C_5H_4)CONH(C_4H_2S)CO_2Me$, with the amido unit at an angle of 3.60 (7)° to the five-atom thienyl group, which is oriented at an angle of 3.17 (7)° to the ester moiety. The primary hydrogen bond is an intramolecular N—H···O=$C_{carboxylate}$ interaction [N···O 2.727 (2) Å], and the main intermolecular hydrogen bond involves a thienyl carboxylate and the carboxylate of a symmetry-related molecule [C···O 3.443 (3) Å].

Comment

Ferrocenyl derivatives have been the subject of much attention in coordination chemistry, given the important roles which they can play, encompassing both structural and electronic capabilities. The integration of ferrocene into new hybrid compounds has greatly expanded the potential and capabilities of new materials with a range of potential applications. Here, we report the synthesis and structure of the title ferrocenoylaminothienyl carboxylate derivative, (I).



(I)

Two views of (I) are depicted, with the atom-numbering scheme, in Figs. 1 and 2. Bond lengths and angles are unexceptional and in accord with anticipated values (Allen, 2002).

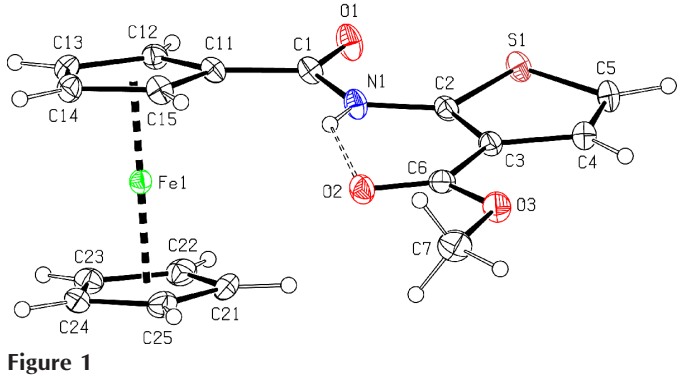


Figure 1
A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular hydrogen bond is shown dashed.

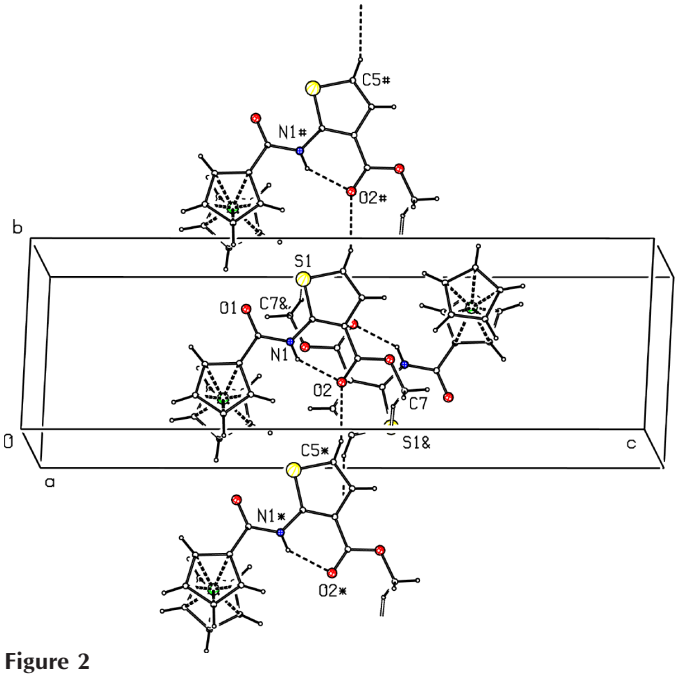


Figure 2
A view of the primary interactions in the crystal structure of (I). Atoms labelled with the suffixes #, * and & are at the symmetry positions (x, 1 + y, z), (x, y − 1, z) and (1 − x, 1 − y, 1 − z), respectively.

The Fe—C bond lengths for the substituted cyclopentadienyl ring of (I) are in the range 2.027 (2)–2.066 (2) Å and are similar to those observed for the unsubstituted ring [2.038 (2)–2.053 (2) Å]. The Fe···*Cg*1 and Fe···*Cg*2 distances are 1.6488 (10) and 1.6535 (10) Å, respectively, and the *Cg*1···Fe1···*Cg*2 angle is 179.36 (5)°, where *Cg*1 and *Cg*2 are the centroids of the substituted and unsubstituted C_5 rings, respectively. The cyclopentadienyl rings deviate slightly from eclipsed geometry, as indicated by the C1*n*···*Cg*1···*Cg*2···C2*n* torsion angles, which are in the range 8.76 (18)–9.46 (17)° (n = 1–5).

The substituted ring system is essentially planar through the amidothienylcarboxylate moiety. The C1/O1/N1/C2 amido moiety is at an angle of 3.60 (7)° to the C2/C3/C4/C5/S1 thienyl ring, which is at an angle of 3.17 (7)° to the C3/C6/C7/O2/O3 ester group. The substituted C_5 ring is at an angle of 12.03 (7)° to the four-atom amido group and 14.10 (6)° to the thienyl ring. Apart from the twisting in the interplanar angles, there is no evidence of bending in these groups due to steric effects, in contrast to 2-(ferrocenyl)thiophene-3-carboxylic acid, where the thienyl ring bonded directly to the ferrocenyl moiety is bent significantly from linearity (Gallagher *et al.*, 2001).

The primary hydrogen-bonding mode in (I) is an intramolecular hydrogen bond involving the amido N—H with the carboxylate O═C group, forming a ring with graph set *S*(6) (Bernstein *et al.*, 1995) and directly influencing the coplanarity of the atoms involved. Molecules of (I) assemble along the *b* axis through a C—H···O═C interaction involving thienyl atom C5 and carboxylate atom O2, as indicated by C5—H5···(O2═C2)# in Fig. 2 [symmetry code: (#) x, 1 + y, z]. A C_{methyl}—H···S contact augments this about inversion centres

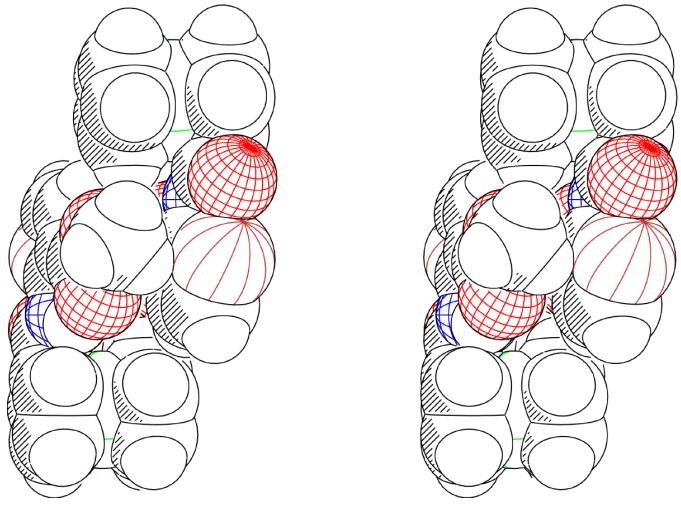
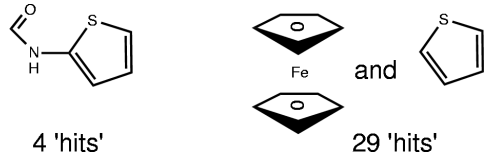


Figure 3
A stereoview of the hydrogen-bonded dimer generated by the C—H···S contact.

as C7—H7···S1& [symmetry code: (&) 1 − x, 1 − y, 1 − z; Figs. 2 and 3]. The closest contact involving atom Fe1 is with C12—H12, as C12—H12···Fe1$ [symmetry code: ($) −$x$, $\frac{1}{2}$ + y, $\frac{1}{2}$ − z], although this is not depicted in Fig. 2. Atom H12 is positioned such that it also forms contacts with the two C_5 ring atoms, C13 and C23. Examination of the structure with *PLATON* (Spek, 2003) showed that there are no solvent accessible voids in the crystal structure.



A search for crystal structures incorporating the amidothienyl fragment [as O═C—N(H)—C_4S] in the Cambridge Structural Database (Version 5.25, July 2004; Allen, 2002) reveals a total of four derivatives (with coordinates). A related search for structures incorporating the ferrocenyl (as C_5FeC_5) and thiophene groups (as C_4S) yields 29 systems (the second scheme shows the structural fragments searched for in the Cambridge Structural Database) (Hudson *et al.*, 2001). In comparison, a search with ferrocene and pyridyl (as C_5N) gives 317 structures, indicating the paucity of data for S-heteroaromatic donors as ligands in ferrocene chemistry when compared with typical heteroaromatic systems containing N donors such as pyridine (Allen, 2002).

Experimental

Methyl 2-*N*-(ferrocenoylamido)-thienyl-3-carboxylate, (I), was synthesized in low yield from the starting materials ferrocene carboxylic acid and methyl 2-aminothienyl-3-carboxylate using standard procedures. Full synthetic details, together with electrochemical studies, will be published in a full paper to follow this structure report.

Crystal data

$[Fe(C_5H_5)(C_{12}H_{10}NO_3S)]$
M_r = 369.21
Monoclinic, $P2_1/c$
a = 7.1714 (4) Å
b = 8.1184 (3) Å
c = 26.4299 (14) Å
β = 95.721 (2)°
V = 1531.09 (13) Å^3
Z = 4
D_x = 1.602 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4398 reflections
θ = 2.6–27.5°
μ = 1.14 mm^{-1}
T = 150 (1) K
Block, red
0.30 × 0.24 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.747, T_{max} = 0.797
6362 measured reflections
3420 independent reflections
2749 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 27.6°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -34 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.079
S = 1.04
3420 reflections
213 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 1.1497P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Extinction correction: none

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.725 (2)	C2—C3	1.381 (3)
S1—C5	1.730 (2)	C3—C4	1.430 (3)
O1—C1	1.232 (2)	C3—C6	1.463 (3)
C1—N1	1.370 (3)	C4—C5	1.348 (3)
C1—C11	1.471 (3)	C6—O2	1.218 (2)
N1—C2	1.376 (3)	C6—O3	1.345 (3)
N1—H1	0.80 (2)	O3—C7	1.446 (3)
C2—S1—C5	90.93 (11)	C2—C3—C6	121.37 (18)
C1—N1—C2	125.81 (19)	C4—C3—C6	126.9 (2)
C1—N1—H1	120.9 (17)	C3—C4—C5	112.7 (2)
C2—N1—H1	113.3 (17)	S1—C5—C4	112.68 (17)
O1—C1—N1	121.1 (2)	O2—C6—O3	123.12 (19)
O1—C1—C11	123.0 (2)	O2—C6—C3	124.9 (2)
N1—C1—C11	115.88 (18)	O3—C6—C3	112.01 (18)
N1—C2—C3	124.49 (19)	C6—O3—C7	115.83 (18)
S1—C2—N1	123.54 (16)	C1—C11—C12	123.62 (18)
S1—C2—C3	111.94 (15)	C1—C11—C15	128.61 (19)
C2—C3—C4	111.75 (19)	C1—C11—Fe1	121.52 (15)
O1—C1—N1—C2	2.1 (4)	O2—C6—O3—C7	0.6 (3)
C1—N1—C2—S1	2.7 (3)	O1—C1—C11—C12	14.8 (3)
N1—C2—C3—C6	1.0 (3)	N1—C1—C11—C15	8.5 (3)
C2—C3—C6—O2	3.6 (3)	O1—C1—C11—Fe1	100.9 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.80 (2)	2.08 (2)	2.727 (2)	137 (2)
C5—H5···O2^{i}	0.95	2.53	3.442 (3)	161
C7—H7*C*···S1^{ii}	0.98	2.89	3.682 (3)	139

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+1$.

The H atom bound to N refined to an N—H distance of 0.80 (2) Å. All H atoms bound to C atoms were treated as riding, with methyl C—H = 0.98 Å and aromatic C—H = 0.95 Å, and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for the remainder.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEX* (McArdle, 1995); software used to prepare material for publication: *PREP8* (Ferguson, 1998).

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