CORE

Acta Crystallographica Section E

## Structure Reports

 OnlineISSN 1600-5368

## Steven Alley, ${ }^{\text {a }}$

John F. Gallagher, ${ }^{\text {a }}{ }^{*}$
Peter T. M. Kenny ${ }^{\text {a* }}$ and
Alan J. Lough ${ }^{\text {b }}$
${ }^{\mathrm{a}}$ School of Chemical Sciences, National Institute for Cellular Biotechnology, Dublin City
University, Dublin 9, Ireland, and ${ }^{\mathbf{b}}$ Department of Chemistry, 80 St. George Street, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Correspondence e-mail: john.gallagher@dcu.ie, peter.kenny@dcu.ie

## Key indicators

Single-crystal X-ray study
$T=150 \mathrm{~K}$
Mean $\sigma(\mathrm{C}-\mathrm{C})=0.003 \AA$
$R$ factor $=0.033$
$w R$ 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.
(C) 2005 International Union of Crystallography Printed in Great Britain - all rights reserved

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

The title compound, $\left[\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)\left(\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{NO}_{3} \mathrm{~S}\right)\right]$, was synthesized from ferrocenecarboxylic acid and methyl 2-aminothio-phene-3-carboxylate in modest yield. The substituted ring system is essentially planar through the amidothienylcarboxylate moiety, $\eta^{5}-\left(\mathrm{C}_{5} \mathrm{H}_{4}\right) \mathrm{CONH}\left(\mathrm{C}_{4} \mathrm{H}_{2} \mathrm{~S}\right) \mathrm{CO}_{2} \mathrm{Me}$, with the amido unit at an angle of $3.60(7)^{\circ}$ to the five-atom thienyl group, which is oriented at an angle of $3.17(7)^{\circ}$ to the ester moiety. The primary hydrogen bond is an intramolecular N $\mathrm{H} \cdots \mathrm{O}=\mathrm{C}_{\text {carboxylate }}$ interaction [ $\mathrm{N} \cdots \mathrm{O} 2.727$ (2) $\AA$ ], and the main intermolecular hydrogen bond involves a thienyl carboxylate and the carboxylate of a symmetry-related molecule [C $\cdots$ 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.

Received 16 November 2004 Accepted 16 December 2004 Online 8 January 2005


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 $\mathrm{Fe}-\mathrm{C}$ bond lengths for the substituted cyclopentadienyl ring of (I) are in the range 2.027 (2)-2.066 (2) $\AA$ and are similar to those observed for the unsubstituted ring [2.038 (2)$2.053(2) \AA]$. The $\mathrm{Fe} \cdots C g 1$ and $\mathrm{Fe} \cdots C g 2$ distances are 1.6488 (10) and $1.6535(10) \AA$, respectively, and the $C g 1 \cdots \mathrm{Fe} 1 \cdots C g 2$ angle is $179.36(5)^{\circ}$, where $C g 1$ and $C g 2$ are the centroids of the substituted and unsubstituted $\mathrm{C}_{5}$ rings, respectively. The cyclopentadienyl rings deviate slightly from eclipsed geometry, as indicated by the C1n..Cg1... $C g 2 \cdots \mathrm{C} 2 n$ torsion angles, which are in the range 8.76 (18)-$9.46(17)^{\circ}(n=1-5)$.

The substituted ring system is essentially planar through the amidothienylcarboxylate moiety. The $\mathrm{C} 1 / \mathrm{O} 1 / \mathrm{N} 1 / \mathrm{C} 2$ amido moiety is at an angle of $3.60(7)^{\circ}$ to the $\mathrm{C} 2 / \mathrm{C} 3 / \mathrm{C} 4 / \mathrm{C} 5 / \mathrm{S} 1$ thienyl ring, which is at an angle of 3.17 (7) ${ }^{\circ}$ to the $\mathrm{C} 3 / \mathrm{C} 6 / \mathrm{C} 7 /$ $\mathrm{O} 2 / \mathrm{O} 3$ ester group. The substituted $\mathrm{C}_{5}$ ring is at an angle of 12.03 (7) ${ }^{\circ}$ to the four-atom amido group and $14.10(6)^{\circ}$ 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 $\mathrm{N}-\mathrm{H}$ with the carboxylate $\mathrm{O}=\mathrm{C}$ 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 $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}=\mathrm{C}$ interaction involving thienyl atom C 5 and carboxylate atom O 2 , as indicated by $\mathrm{C} 5-$ $\mathrm{H} 5 \cdots(\mathrm{O} 2=\mathrm{C} 2) \#$ in Fig. 2 [symmetry code: (\#) $x, 1+y, z$ ]. A $\mathrm{C}_{\text {methyl }}-\mathrm{H} \cdots \mathrm{S}$ contact augments this about inversion centres


Figure 3
A stereoview of the hydrogen-bonded dimer generated by the $\mathrm{C}-\mathrm{H} \cdots \mathrm{S}$ contact.
as C7-H7‥S1\& [symmetry code: (\&) $1-x, 1-y, 1-z$; Figs. 2 and 3]. The closest contact involving atom Fe 1 is with $\mathrm{C} 12-\mathrm{H} 12$, as $\mathrm{C} 12-\mathrm{H} 12 \cdots \mathrm{Fe} 1 \$$ [symmetry code: $(\$)-x, \frac{1}{2}+y$, $\left.\frac{1}{2}-z\right]$, although this is not depicted in Fig. 2. Atom H12 is positioned such that it also forms contacts with the two $\mathrm{C}_{5}$ 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 $\mathrm{O}=\mathrm{C}-\mathrm{N}(\mathrm{H})-\mathrm{C}_{4} \mathrm{~S}$ ] 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 $\mathrm{C}_{5} \mathrm{FeC}_{5}$ ) and thiophene groups (as $\mathrm{C}_{4} \mathrm{~S}$ ) 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 $\mathrm{C}_{5} \mathrm{~N}$ ) 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

$\left[\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)\left(\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{NO}_{3} \mathrm{~S}\right)\right]$
$M_{r}=369.21$
Monoclinic, $P 2_{1} / c$
$a=7.1714$ (4) $\AA$
$b=8.1184(3) \AA$
$c=26.4299$ (14) $\AA$
$\beta=95.721(2)^{\circ}$
$V=1531.09(13) \AA^{3}$
$Z=4$
$D_{x}=1.602 \mathrm{Mg} \mathrm{m}^{-3}$
Mo $K \alpha$ radiation
Cell parameters from 4398
reflections
$\theta=2.6-27.5^{\circ}$
$\mu=1.14 \mathrm{~mm}^{-1}$
$T=150$ (1) K
Block, red
$0.30 \times 0.24 \times 0.20 \mathrm{~mm}$

## Data collection

Nonius KappaCCD diffractometer $\varphi$ scans, and $\omega$ scans with $\kappa$ offsets Absorption correction: multi-scan
(DENZO-SMN; Otwinowski \&
Minor, 1997)
$T_{\text {min }}=0.747, T_{\text {max }}=0.797$
6362 measured reflections

## Refinement

Refinement on $F^{2}$
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.033$
$w R\left(F^{2}\right)=0.079$
$S=1.04$
3420 reflections
213 parameters
H atoms treated by a mixture of independent and constrained refinement

3420 independent reflections 2749 reflections with $I>2 \sigma(I)$
$R_{\text {int }}=0.030$
$\theta_{\text {max }}=27.6^{\circ}$
$h=-9 \rightarrow 9$
$k=-10 \rightarrow 10$
$l=-34 \rightarrow 34$

$$
\begin{aligned}
& w=1 /\left[\sigma^{2}\left(F_{\mathrm{o}}{ }^{2}\right)+(0.022 P)^{2}\right. \\
& +1.1497 P] \\
& \text { where } P=\left(F_{\mathrm{o}}{ }^{2}+2 F_{\mathrm{c}}{ }^{2}\right) / 3 \\
& (\Delta / \sigma)_{\max }=0.001 \text { 。 } \\
& \Delta \rho_{\text {max }}=0.29 \mathrm{e}^{-3} \\
& \Delta \rho_{\min }=-0.35 \mathrm{e} \mathrm{~A}^{-3} \\
& \text { Extinction correction: none }
\end{aligned}
$$

Table 1
Selected geometric parameters ( $\left(\AA,{ }^{\circ}\right.$ ).

| S1-C2 | $1.725(2)$ | $\mathrm{C} 2-\mathrm{C} 3$ | $1.381(3)$ |
| :--- | :---: | :--- | ---: |
| $\mathrm{S} 1-\mathrm{C} 5$ | $1.730(2)$ | $\mathrm{C} 3-\mathrm{C} 4$ | $1.430(3)$ |
| $\mathrm{O} 1-\mathrm{C} 1$ | $1.232(2)$ | $\mathrm{C} 3-\mathrm{C} 6$ | $1.463(3)$ |
| $\mathrm{C} 1-\mathrm{N} 1$ | $1.370(3)$ | $\mathrm{C} 4-\mathrm{C} 5$ | $1.348(3)$ |
| $\mathrm{C} 1-\mathrm{C} 11$ | $1.471(3)$ | $\mathrm{C} 6-\mathrm{O} 2$ | $1.218(2)$ |
| $\mathrm{N} 1-\mathrm{C} 2$ | $1.376(3)$ | $\mathrm{C} 6-\mathrm{O} 3$ | $1.345(3)$ |
| $\mathrm{N} 1-\mathrm{H} 1$ | $0.80(2)$ | $\mathrm{O} 3-\mathrm{C} 7$ | $1.446(3)$ |
|  |  |  |  |
| $\mathrm{C} 2-\mathrm{S} 1-\mathrm{C} 5$ | $90.93(11)$ | $\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 6$ | $121.37(18)$ |
| $\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 2$ | $125.81(19)$ | $\mathrm{C} 4-\mathrm{C} 3-\mathrm{C} 6$ | $126.9(2)$ |
| $\mathrm{C} 1-\mathrm{N} 1-\mathrm{H} 1$ | $120.9(17)$ | $\mathrm{C} 3-\mathrm{C} 4-\mathrm{C} 5$ | $112.7(2)$ |
| $\mathrm{C} 2-\mathrm{N} 1-\mathrm{H} 1$ | $113.3(17)$ | $\mathrm{S} 1-\mathrm{C} 5-\mathrm{C} 4$ | $112.68(17)$ |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{N} 1$ | $121.1(2)$ | $\mathrm{O} 2-\mathrm{C} 6-\mathrm{O} 3$ | $123.12(19)$ |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 11$ | $123.0(2)$ | $\mathrm{O} 2-\mathrm{C} 6-\mathrm{C} 3$ | $124.9(2)$ |
| N1-C1-C11 | $115.88(18)$ | $\mathrm{O} 3-\mathrm{C} 6-\mathrm{C} 3$ | $112.01(18)$ |
| N1-C2-C3 | $124.49(19)$ | $\mathrm{C} 6-\mathrm{O} 3-\mathrm{C} 7$ | $115.83(18)$ |
| $\mathrm{S} 1-\mathrm{C} 2-\mathrm{N} 1$ | $123.54(16)$ | $\mathrm{C} 1-\mathrm{C} 11-\mathrm{C} 12$ | $123.62(18)$ |
| $\mathrm{S} 1-\mathrm{C} 2-\mathrm{C} 3$ | $111.94(15)$ | $\mathrm{C} 1-\mathrm{C} 11-\mathrm{C} 15$ | $128.61(19)$ |
| $\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4$ | $111.75(19)$ | $\mathrm{C} 1-\mathrm{C} 11-\mathrm{Fe} 1$ | $121.52(15)$ |
|  |  |  |  |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 2$ | $2.1(4)$ | $\mathrm{O} 2-\mathrm{C} 6-\mathrm{O} 3-\mathrm{C} 7$ | $0.6(3)$ |
| $\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 2-\mathrm{S} 1$ | $2.7(3)$ | $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 11-\mathrm{C} 12$ | $14.8(3)$ |
| N1-C2-C3-C6 | $1.0(3)$ | $\mathrm{N} 1-\mathrm{C} 1-\mathrm{C} 11-\mathrm{C} 15$ | $8.5(3)$ |
| $\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 6-\mathrm{O} 2$ | $3.6(3)$ | $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 11-\mathrm{Fe} 1$ | $100.9(2)$ |

Table 2
Hydrogen-bond geometry ( $\mathrm{A},{ }^{\circ}$ ).

| $D-\mathrm{H} \cdots A$ | $D-\mathrm{H}$ | $\mathrm{H} \cdots A$ | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{~N} 1-\mathrm{H} 1 \cdots \mathrm{O} 2$ | $0.80(2)$ | $2.08(2)$ | $2.727(2)$ | $137(2)$ |
| $\mathrm{C} 5-\mathrm{H} 5 \cdots \mathrm{O} 2^{\mathrm{i}}$ | 0.95 | 2.53 | $3.442(3)$ | 161 |
| $\mathrm{C} 7-\mathrm{H} 7 C \cdots \mathrm{~S}^{\mathrm{ii}}$ | 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 $\mathrm{N}-\mathrm{H}$ distance of 0.80 (2) $\AA$. All H atoms bound to C atoms were treated as riding, with methyl $\mathrm{C}-\mathrm{H}=0.98 \AA$ and aromatic $\mathrm{C}-\mathrm{H}=0.95 \AA$, and with $U_{\text {iso }}(\mathrm{H})=$ $1.5 U_{\mathrm{eq}}(\mathrm{C})$ for methyl H atoms and $1.2 U_{\mathrm{eq}}(\mathrm{C})$ 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).

SA, JFG and PTMK thank Dublin City University and the Department of Education, Ireland, for funding the National Institute for Cellular Biotechnology (PRTLI programme, round 3, 2001-2008).

## References

Allen, F. H. (2002). Acta Cryst. B58, 380-388.
Bernstein, J., Davies, R. E., Shimoni, L. \& Chang, N.-L. (1995). Angew. Chem. Int. Ed. Engl. 34, 1555-1573.
Ferguson, G. (1998). PREP8. University of Guelph, Canada.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. \& White, P. S. (1989). J. Appl. Cryst. 22, 384-387.
Gallagher, J. F., Hudson, R. D. A. \& Manning, A. R. (2001). Acta Cryst. C57, 28-30.
Hudson, R. D. A., Asselsbergh, I., Clays, K., Cuffe, L. P., Gallagher, J. F., Manning, A. R., Persoons, A. \& Wostyn, K. (2001). J. Organomet. Chem. 637, 435-444.
McArdle, P. (1995). J. Appl. Cryst. 28, 65-65.
Nonius (1997). KappaCCD Server Software. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. \& Minor W. (1997). Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, edited by C. W. Carter Jr. \& R. M. Sweet, pp. 307-326. New York: Academic Press.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
Spek, A. L. (2003). J. Appl. Cryst. 36, 7-13.

