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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 = 16.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

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

The title compound, [Fe(C₅H₅)(C₁₂H₁₀NO₃S)], was synthesized from ferrocenecarboxylic acid and methyl 2-aminothiophene-3-carboxylate in modest yield. The substituted ring system is essentially planar through the amidothiencylcarboxylate moiety, η^5 -(C₅H₄)CONH(C₄H₂S)CO₂Me, 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].

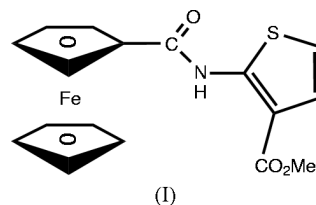
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Comment

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 ferrocenylaminothienyl carboxylate derivative, (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).

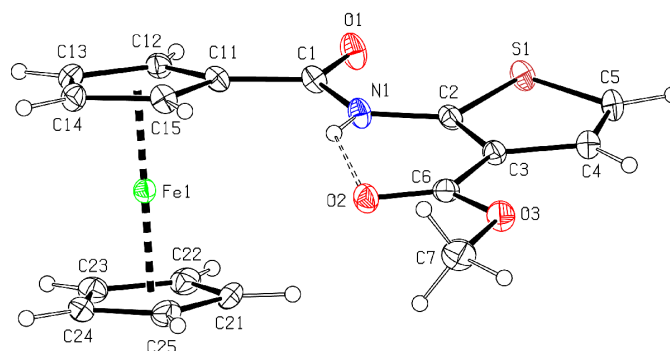
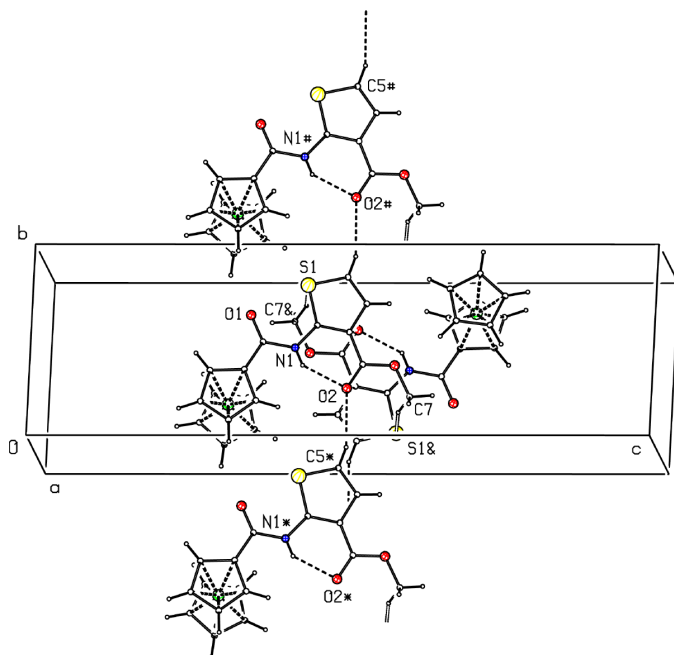


Figure 1

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.

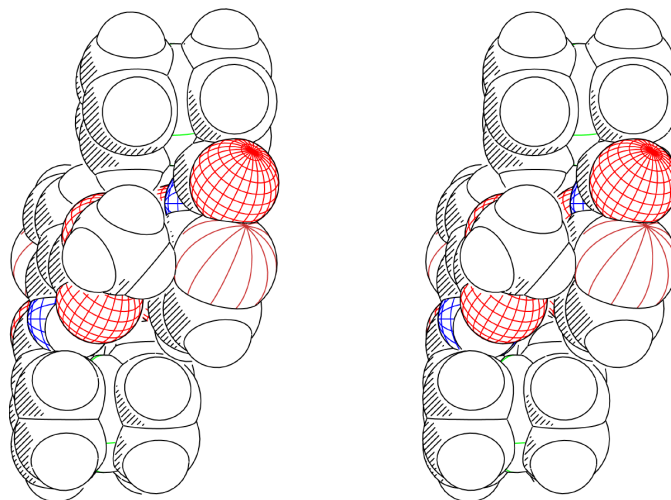

Figure 2

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···Cg1 and Fe···Cg2 distances are 1.6488 (10) and 1.6535 (10) Å, respectively, and the Cg1···Fe1···Cg2 angle is 179.36 (5)°, where Cg1 and Cg2 are the centroids of the substituted and unsubstituted C₅ rings, respectively. The cyclopentadienyl rings deviate slightly from eclipsed geometry, as indicated by the C1n···Cg1···Cg2···C2n torsion angles, which are in the range 8.76 (18)–9.46 (17)° ($n = 1-5$).

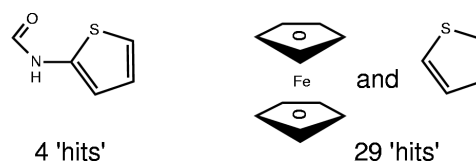
The substituted ring system is essentially planar through the amidothiénylcarboxylate moiety. The C1/O1/N1/C2 amido moiety is at an angle of 3.60 (7)° to the C2/C3/C4/C5/S1 thienyl ring, which is at an angle of 3.17 (7)° to the C3/C6/C7/O2/O3 ester group. The substituted C₅ ring is at an angle of 12.03 (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 C₅ 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 amidothiényl fragment [as O=C—N(H)—C₄S] 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 C₅FeC₅) and thiophene groups (as C₄S) 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 C₅N) 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(C₅H₅)(C₁₂H₁₀NO₃S)]
M_r = 369.21
 Monoclinic, *P*₂₁/*c*
a = 7.1714 (4) Å
b = 8.1184 (3) Å
c = 26.4299 (14) Å
 β = 95.721 (2)°
V = 1531.09 (13) Å³
Z = 4

D_x = 1.602 Mg m⁻³
 Mo *K*α 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* > 2σ(*I*)
R_{int} = 0.030
 θ_{\max} = 27.6°
h = -9 → 9
k = -10 → 10
l = -34 → 34

Refinement

Refinement on *F*²
R[*F*² > 2σ(*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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e \AA}^{-3}$
 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, °).

<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>
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–H7C···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) = 1.5*U*_{eq}(C) for methyl H atoms and 1.2*U*_{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 *ORTEP* (McArdle, 1995); software used to prepare material for publication: *PREP8* (Ferguson, 1998).

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supporting information

Acta Cryst. (2005). E61, m201–m203 [https://doi.org/10.1107/S1600536804033355]

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Crystal data

[Fe(C₅H₅)(C₁₂H₁₀NO₃S)]

$M_r = 369.21$

Monoclinic, $P2_1/c$

Hall symbol: -p 2ybc

$a = 7.1714$ (4) Å

$b = 8.1184$ (3) Å

$c = 26.4299$ (14) Å

$\beta = 95.721$ (2)°

$V = 1531.09$ (13) Å³

$Z = 4$

$F(000) = 760$

$D_x = 1.602$ Mg m⁻³

Melting point: 406 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4398 reflections

$\theta = 2.6$ – 27.5 °

$\mu = 1.14$ mm⁻¹

$T = 294$ K

Block, red

$0.30 \times 0.24 \times 0.20$ mm

Data collection

Kappa-CCD

diffractometer

Radiation source: fine-focus sealed X-ray tube

Graphite monochromator

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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 27.6$ °, $\theta_{\min} = 2.6$ °

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -34 \rightarrow 34$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.079$

$S = 1.04$

3420 reflections

213 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

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

Special details

Experimental. ? #Insert any special details here.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Planes data #####

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$-7.0757(0.0013)x + 0.8840(0.0089)y + 5.7824(0.0286)z = 2.4878(0.0093)$

* 0.0015 (0.0014) C11 * -0.0011 (0.0014) C12 * 0.0003 (0.0014) C13 * 0.0007 (0.0014) C14 * -0.0013 (0.0014) C15 - 1.6484 (0.0010) Fe1 - 0.1950 (0.0065) S1

Rms deviation of fitted atoms = 0.0011

$7.0858(0.0014)x - 0.9118(0.0096)y - 5.3747(0.0304)z = 0.9389(0.0099)$

Angle to previous plane (with approximate e.s.d.) = 0.92 (5)

* -0.0005 (0.0014) C21 * -0.0007 (0.0014) C22 * 0.0015 (0.0014) C23 * -0.0018 (0.0014) C24 * 0.0014 (0.0014) C25 - 1.6533 (0.0010) Fe1 - 3.0752 (0.0069) S1

Rms deviation of fitted atoms = 0.0013

$-6.7929(0.0022)x + 0.3781(0.0143)y + 10.8365(0.0210)z = 4.0157(0.0125)$

Angle to previous plane (with approximate e.s.d.) = 12.95 (7)

* 0.0078 (0.0013) C1 * -0.0039 (0.0007) O1 * -0.0076 (0.0013) N1 * 0.0037 (0.0006) C2 - 1.6307 (0.0057) Fe1 0.1081 (0.0041) S1

Rms deviation of fitted atoms = 0.0061

$-6.7724(0.0020)x - 0.1234(0.0081)y + 11.1286(0.0203)z = 3.8475(0.0129)$

Angle to previous plane (with approximate e.s.d.) = 3.60 (7)

* 0.0021 (0.0012) C2 * -0.0019 (0.0014) C3 * 0.0005 (0.0015) C4 * 0.0008 (0.0013) C5 * -0.0015 (0.0010) S1

Rms deviation of fitted atoms = 0.0015

$-6.8893(0.0018)x - 0.2013(0.0083)y + 9.8050(0.0219)z = 3.1076(0.0132)$

Angle to previous plane (with approximate e.s.d.) = 3.17 (7)

* -0.0013 (0.0011) C3 * -0.0011 (0.0018) C6 * -0.0023 (0.0011) C7 * 0.0012 (0.0007) O2 * 0.0035 (0.0015) O3 - 1.1763 (0.0056) Fe1 0.0819 (0.0039) S1

Rms deviation of fitted atoms = 0.0021

Distances #####

Distance M·O

3.8706 (0.0015) Fe1 - O1 4.9649 (0.0016) Fe1 - O2 7.0874 (0.0016) Fe1 - O3

Distance M·S

5.9696 (0.0006) Fe1 - S1

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.16371 (4)	0.19319 (3)	0.315967 (11)	0.02178 (10)
S1	0.13405 (8)	0.81350 (6)	0.43619 (2)	0.02950 (14)
O1	0.0049 (2)	0.63043 (18)	0.35130 (6)	0.0356 (4)
C1	0.0283 (3)	0.4947 (3)	0.37176 (8)	0.0265 (5)
N1	0.1081 (3)	0.4804 (2)	0.42088 (7)	0.0269 (4)
C2	0.1645 (3)	0.6090 (2)	0.45275 (8)	0.0244 (4)
C3	0.2463 (3)	0.5907 (2)	0.50198 (8)	0.0247 (4)
C4	0.2831 (3)	0.7463 (3)	0.52632 (9)	0.0311 (5)
C5	0.2306 (3)	0.8747 (3)	0.49581 (9)	0.0335 (5)
C6	0.2829 (3)	0.4276 (3)	0.52436 (8)	0.0264 (5)
O2	0.2543 (2)	0.29772 (17)	0.50188 (6)	0.0304 (4)
O3	0.3519 (2)	0.43670 (18)	0.57351 (6)	0.0332 (4)

C7	0.3932 (4)	0.2810 (3)	0.59872 (10)	0.0409 (6)
C11	-0.0268 (3)	0.3392 (2)	0.34582 (8)	0.0254 (5)
C12	-0.0719 (3)	0.3256 (2)	0.29233 (8)	0.0255 (5)
C13	-0.1029 (3)	0.1574 (3)	0.28034 (8)	0.0277 (5)
C14	-0.0771 (3)	0.0647 (3)	0.32608 (8)	0.0284 (5)
C15	-0.0296 (3)	0.1759 (3)	0.36684 (8)	0.0275 (5)
C21	0.4260 (3)	0.2832 (3)	0.33899 (10)	0.0347 (5)
C22	0.3873 (3)	0.2982 (3)	0.28540 (10)	0.0343 (5)
C23	0.3515 (3)	0.1381 (3)	0.26496 (9)	0.0339 (5)
C24	0.3676 (3)	0.0246 (3)	0.30608 (9)	0.0334 (5)
C25	0.4142 (3)	0.1139 (3)	0.35174 (10)	0.0353 (5)
H1	0.127 (3)	0.392 (3)	0.4336 (9)	0.027 (6)*
H4	0.3385	0.7580	0.5603	0.037*
H5	0.2450	0.9866	0.5060	0.040*
H7A	0.2761	0.2212	0.6018	0.061*
H7B	0.4572	0.3009	0.6327	0.061*
H7C	0.4742	0.2153	0.5788	0.061*
H12	-0.0797	0.4142	0.2687	0.031*
H13	-0.1354	0.1138	0.2473	0.033*
H14	-0.0895	-0.0513	0.3289	0.034*
H15	-0.0043	0.1475	0.4017	0.033*
H21	0.4548	0.3710	0.3622	0.042*
H22	0.3856	0.3979	0.2665	0.041*
H23	0.3220	0.1117	0.2301	0.041*
H24	0.3502	-0.0912	0.3035	0.040*
H25	0.4339	0.0685	0.3850	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.02385 (17)	0.01945 (16)	0.02158 (16)	0.00004 (12)	0.00008 (11)	-0.00039 (12)
S1	0.0384 (3)	0.0188 (3)	0.0318 (3)	0.0011 (2)	0.0062 (2)	0.0011 (2)
O1	0.0568 (11)	0.0212 (8)	0.0286 (8)	0.0034 (8)	0.0031 (7)	0.0018 (6)
C1	0.0316 (12)	0.0237 (11)	0.0247 (11)	0.0032 (9)	0.0058 (9)	-0.0007 (8)
N1	0.0377 (11)	0.0176 (9)	0.0253 (10)	0.0012 (8)	0.0027 (8)	0.0004 (7)
C2	0.0258 (11)	0.0191 (10)	0.0293 (11)	0.0010 (8)	0.0079 (9)	-0.0001 (8)
C3	0.0245 (11)	0.0207 (10)	0.0292 (11)	0.0004 (8)	0.0043 (9)	-0.0015 (8)
C4	0.0312 (12)	0.0277 (11)	0.0339 (13)	-0.0007 (10)	0.0006 (10)	-0.0068 (10)
C5	0.0390 (14)	0.0209 (11)	0.0404 (14)	-0.0023 (10)	0.0025 (11)	-0.0080 (10)
C6	0.0217 (11)	0.0277 (11)	0.0299 (11)	0.0017 (9)	0.0031 (9)	0.0002 (9)
O2	0.0355 (9)	0.0209 (8)	0.0343 (9)	0.0019 (7)	0.0000 (7)	-0.0005 (6)
O3	0.0385 (9)	0.0287 (8)	0.0307 (9)	0.0052 (7)	-0.0058 (7)	0.0017 (7)
C7	0.0416 (15)	0.0358 (14)	0.0433 (15)	0.0072 (11)	-0.0061 (11)	0.0099 (11)
C11	0.0287 (12)	0.0212 (10)	0.0269 (11)	0.0032 (8)	0.0056 (9)	0.0002 (8)
C12	0.0266 (11)	0.0241 (11)	0.0252 (11)	0.0034 (9)	-0.0004 (9)	0.0015 (8)
C13	0.0242 (11)	0.0305 (12)	0.0275 (11)	-0.0004 (9)	-0.0025 (9)	-0.0034 (9)
C14	0.0294 (12)	0.0222 (10)	0.0345 (12)	-0.0054 (9)	0.0068 (10)	-0.0005 (9)
C15	0.0340 (13)	0.0256 (11)	0.0237 (11)	0.0003 (9)	0.0074 (9)	0.0027 (8)

C21	0.0239 (12)	0.0312 (13)	0.0469 (14)	-0.0038 (9)	-0.0066 (10)	-0.0077 (10)
C22	0.0262 (12)	0.0327 (12)	0.0450 (14)	-0.0042 (10)	0.0075 (10)	0.0035 (11)
C23	0.0268 (12)	0.0415 (13)	0.0343 (13)	0.0010 (10)	0.0079 (10)	-0.0056 (10)
C24	0.0262 (12)	0.0260 (12)	0.0470 (14)	0.0048 (9)	-0.0014 (10)	-0.0062 (10)
C25	0.0277 (12)	0.0333 (12)	0.0423 (14)	0.0045 (10)	-0.0093 (10)	0.0016 (10)

Geometric parameters (Å, °)

Fe1—C11	2.027 (2)	C2—C3	1.381 (3)
Fe1—C12	2.047 (2)	C3—C4	1.430 (3)
Fe1—C13	2.066 (2)	C3—C6	1.463 (3)
Fe1—C14	2.058 (2)	C4—C5	1.348 (3)
Fe1—C15	2.030 (2)	C6—O2	1.218 (2)
Fe1—C21	2.053 (2)	C6—O3	1.345 (3)
Fe1—C22	2.051 (2)	O3—C7	1.446 (3)
Fe1—C23	2.047 (2)	C11—C12	1.423 (3)
Fe1—C24	2.038 (2)	C11—C15	1.439 (3)
Fe1—C25	2.048 (2)	C12—C13	1.414 (3)
S1—C2	1.725 (2)	C13—C14	1.420 (3)
S1—C5	1.730 (2)	C14—C15	1.421 (3)
O1—C1	1.232 (2)	C21—C22	1.421 (3)
C1—N1	1.370 (3)	C21—C25	1.419 (3)
C1—C11	1.471 (3)	C22—C23	1.421 (3)
N1—C2	1.376 (3)	C23—C24	1.421 (3)
N1—H1	0.80 (2)	C24—C25	1.419 (3)
C11—Fe1—C15	41.53 (8)	O1—C1—N1	121.1 (2)
C11—Fe1—C24	164.24 (9)	O1—C1—C11	123.0 (2)
C15—Fe1—C24	125.77 (9)	N1—C1—C11	115.88 (18)
C11—Fe1—C12	40.87 (8)	N1—C2—C3	124.49 (19)
C15—Fe1—C12	68.96 (9)	S1—C2—N1	123.54 (16)
C24—Fe1—C12	153.41 (9)	S1—C2—C3	111.94 (15)
C11—Fe1—C23	153.75 (9)	C2—C3—C4	111.75 (19)
C15—Fe1—C23	163.40 (9)	C2—C3—C6	121.37 (18)
C24—Fe1—C23	40.69 (9)	C4—C3—C6	126.9 (2)
C12—Fe1—C23	119.39 (9)	C3—C4—C5	112.7 (2)
C11—Fe1—C25	126.74 (9)	S1—C5—C4	112.68 (17)
C15—Fe1—C25	107.34 (10)	O2—C6—O3	123.12 (19)
C24—Fe1—C25	40.63 (9)	O2—C6—C3	124.9 (2)
C12—Fe1—C25	164.79 (9)	O3—C6—C3	112.01 (18)
C23—Fe1—C25	68.37 (10)	C6—O3—C7	115.83 (18)
C11—Fe1—C22	119.58 (9)	C1—C11—C12	123.62 (18)
C15—Fe1—C22	154.39 (9)	C1—C11—C15	128.61 (19)
C24—Fe1—C22	68.27 (10)	C12—C11—C15	107.55 (18)
C12—Fe1—C22	108.37 (9)	C12—C11—Fe1	70.30 (12)
C23—Fe1—C22	40.57 (9)	C15—C11—Fe1	69.34 (12)
C25—Fe1—C22	68.20 (10)	C1—C11—Fe1	121.52 (15)
C11—Fe1—C21	108.05 (9)	C13—C12—C11	108.23 (18)

C15—Fe1—C21	119.64 (10)	C13—C12—Fe1	70.60 (12)
C24—Fe1—C21	68.23 (9)	C11—C12—Fe1	68.83 (12)
C12—Fe1—C21	127.41 (9)	C12—C13—C14	108.46 (19)
C23—Fe1—C21	68.25 (10)	C12—C13—Fe1	69.17 (12)
C25—Fe1—C21	40.50 (9)	C14—C13—Fe1	69.55 (12)
C22—Fe1—C21	40.52 (10)	C13—C14—C15	108.03 (18)
C11—Fe1—C14	68.84 (9)	C13—C14—Fe1	70.15 (12)
C15—Fe1—C14	40.67 (8)	C15—C14—Fe1	68.62 (12)
C24—Fe1—C14	107.36 (9)	C14—C15—C11	107.72 (19)
C12—Fe1—C14	68.16 (9)	C14—C15—Fe1	70.71 (12)
C23—Fe1—C14	126.18 (9)	C11—C15—Fe1	69.13 (12)
C25—Fe1—C14	119.31 (9)	C25—C21—C22	108.0 (2)
C22—Fe1—C14	163.91 (9)	C25—C21—Fe1	69.58 (13)
C21—Fe1—C14	153.90 (10)	C22—C21—Fe1	69.69 (13)
C11—Fe1—C13	68.32 (9)	C23—C22—C21	108.1 (2)
C15—Fe1—C13	68.29 (9)	C23—C22—Fe1	69.57 (13)
C24—Fe1—C13	119.36 (9)	C21—C22—Fe1	69.79 (13)
C12—Fe1—C13	40.23 (8)	C24—C23—C22	107.7 (2)
C23—Fe1—C13	107.98 (9)	C24—C23—Fe1	69.31 (13)
C25—Fe1—C13	153.56 (9)	C22—C23—Fe1	69.86 (13)
C22—Fe1—C13	127.08 (9)	C25—C24—C23	108.3 (2)
C21—Fe1—C13	164.62 (9)	C25—C24—Fe1	70.06 (13)
C14—Fe1—C13	40.30 (8)	C23—C24—Fe1	70.00 (13)
C2—S1—C5	90.93 (11)	C24—C25—C21	107.9 (2)
C1—N1—C2	125.81 (19)	C24—C25—Fe1	69.31 (13)
C1—N1—H1	120.9 (17)	C21—C25—Fe1	69.92 (13)
C2—N1—H1	113.3 (17)		
O1—C1—N1—C2	2.1 (4)	Fe1—C11—C15—C14	-60.46 (15)
C11—C1—N1—C2	-177.78 (19)	C12—C11—C15—Fe1	60.19 (15)
C1—N1—C2—C3	-179.3 (2)	C1—C11—C15—Fe1	-114.5 (2)
C1—N1—C2—S1	2.7 (3)	C11—Fe1—C15—C14	118.59 (19)
C5—S1—C2—N1	177.87 (19)	C24—Fe1—C15—C14	-74.09 (16)
C5—S1—C2—C3	-0.30 (18)	C12—Fe1—C15—C14	80.57 (14)
N1—C2—C3—C4	-177.8 (2)	C23—Fe1—C15—C14	-42.8 (4)
S1—C2—C3—C4	0.4 (2)	C25—Fe1—C15—C14	-115.06 (14)
N1—C2—C3—C6	1.0 (3)	C22—Fe1—C15—C14	169.35 (19)
S1—C2—C3—C6	179.11 (16)	C21—Fe1—C15—C14	-157.42 (13)
C2—C3—C4—C5	-0.2 (3)	C13—Fe1—C15—C14	37.23 (13)
C6—C3—C4—C5	-178.9 (2)	C24—Fe1—C15—C11	167.32 (13)
C3—C4—C5—S1	0.0 (3)	C12—Fe1—C15—C11	-38.03 (12)
C2—S1—C5—C4	0.17 (19)	C23—Fe1—C15—C11	-161.4 (3)
C2—C3—C6—O2	3.6 (3)	C25—Fe1—C15—C11	126.34 (13)
C4—C3—C6—O2	-177.8 (2)	C22—Fe1—C15—C11	50.8 (3)
C2—C3—C6—O3	-176.03 (19)	C21—Fe1—C15—C11	83.99 (15)
C4—C3—C6—O3	2.5 (3)	C14—Fe1—C15—C11	-118.59 (19)
O2—C6—O3—C7	0.6 (3)	C13—Fe1—C15—C11	-81.36 (13)
C3—C6—O3—C7	-179.72 (19)	C11—Fe1—C21—C25	125.96 (15)

O1—C1—C11—C12	14.8 (3)	C15—Fe1—C21—C25	82.05 (16)
N1—C1—C11—C12	-165.4 (2)	C24—Fe1—C21—C25	-37.74 (15)
O1—C1—C11—C15	-171.4 (2)	C12—Fe1—C21—C25	167.19 (14)
N1—C1—C11—C15	8.5 (3)	C23—Fe1—C21—C25	-81.71 (15)
O1—C1—C11—Fe1	100.9 (2)	C22—Fe1—C21—C25	-119.3 (2)
N1—C1—C11—Fe1	-79.2 (2)	C14—Fe1—C21—C25	47.4 (3)
C15—Fe1—C11—C12	-118.51 (18)	C13—Fe1—C21—C25	-160.3 (3)
C24—Fe1—C11—C12	-159.5 (3)	C11—Fe1—C21—C22	-114.71 (14)
C23—Fe1—C11—C12	49.6 (3)	C15—Fe1—C21—C22	-158.62 (13)
C25—Fe1—C11—C12	167.86 (13)	C24—Fe1—C21—C22	81.59 (15)
C22—Fe1—C11—C12	84.13 (15)	C12—Fe1—C21—C22	-73.48 (16)
C21—Fe1—C11—C12	126.87 (13)	C23—Fe1—C21—C22	37.62 (14)
C14—Fe1—C11—C12	-80.67 (13)	C25—Fe1—C21—C22	119.3 (2)
C13—Fe1—C11—C12	-37.23 (12)	C14—Fe1—C21—C22	166.72 (18)
C24—Fe1—C11—C15	-41.0 (4)	C13—Fe1—C21—C22	-41.0 (4)
C12—Fe1—C11—C15	118.51 (18)	C25—C21—C22—C23	0.0 (3)
C23—Fe1—C11—C15	168.12 (19)	Fe1—C21—C22—C23	-59.25 (16)
C25—Fe1—C11—C15	-73.63 (16)	C25—C21—C22—Fe1	59.23 (16)
C22—Fe1—C11—C15	-157.36 (13)	C11—Fe1—C22—C23	-157.33 (14)
C21—Fe1—C11—C15	-114.61 (14)	C15—Fe1—C22—C23	166.48 (19)
C14—Fe1—C11—C15	37.85 (13)	C24—Fe1—C22—C23	37.85 (14)
C13—Fe1—C11—C15	81.28 (14)	C12—Fe1—C22—C23	-114.03 (14)
C15—Fe1—C11—C1	123.4 (2)	C25—Fe1—C22—C23	81.76 (15)
C24—Fe1—C11—C1	82.5 (4)	C21—Fe1—C22—C23	119.3 (2)
C12—Fe1—C11—C1	-118.0 (2)	C14—Fe1—C22—C23	-39.3 (4)
C23—Fe1—C11—C1	-68.4 (3)	C13—Fe1—C22—C23	-73.27 (17)
C25—Fe1—C11—C1	49.8 (2)	C11—Fe1—C22—C21	83.34 (15)
C22—Fe1—C11—C1	-33.9 (2)	C15—Fe1—C22—C21	47.1 (3)
C21—Fe1—C11—C1	8.82 (19)	C24—Fe1—C22—C21	-81.48 (14)
C14—Fe1—C11—C1	161.28 (19)	C12—Fe1—C22—C21	126.64 (13)
C13—Fe1—C11—C1	-155.28 (19)	C23—Fe1—C22—C21	-119.3 (2)
C15—C11—C12—C13	0.2 (2)	C25—Fe1—C22—C21	-37.57 (14)
C1—C11—C12—C13	175.2 (2)	C14—Fe1—C22—C21	-158.6 (3)
Fe1—C11—C12—C13	59.83 (15)	C13—Fe1—C22—C21	167.40 (13)
C15—C11—C12—Fe1	-59.58 (15)	C21—C22—C23—C24	0.2 (3)
C1—C11—C12—Fe1	115.4 (2)	Fe1—C22—C23—C24	-59.18 (15)
C11—Fe1—C12—C13	-119.47 (18)	C21—C22—C23—Fe1	59.38 (16)
C15—Fe1—C12—C13	-80.85 (14)	C11—Fe1—C23—C24	168.31 (19)
C24—Fe1—C12—C13	48.3 (3)	C15—Fe1—C23—C24	-40.2 (4)
C23—Fe1—C12—C13	83.27 (15)	C12—Fe1—C23—C24	-156.80 (13)
C25—Fe1—C12—C13	-159.4 (3)	C25—Fe1—C23—C24	37.73 (13)
C22—Fe1—C12—C13	126.24 (14)	C22—Fe1—C23—C24	119.0 (2)
C21—Fe1—C12—C13	167.27 (14)	C21—Fe1—C23—C24	81.46 (14)
C14—Fe1—C12—C13	-37.01 (13)	C14—Fe1—C23—C24	-73.52 (17)
C15—Fe1—C12—C11	38.63 (12)	C13—Fe1—C23—C24	-114.40 (14)
C24—Fe1—C12—C11	167.72 (19)	C11—Fe1—C23—C22	49.3 (3)
C23—Fe1—C12—C11	-157.26 (13)	C15—Fe1—C23—C22	-159.3 (3)
C25—Fe1—C12—C11	-40.0 (4)	C24—Fe1—C23—C22	-119.0 (2)

C22—Fe1—C12—C11	-114.29 (13)	C12—Fe1—C23—C22	84.16 (16)
C21—Fe1—C12—C11	-73.26 (16)	C25—Fe1—C23—C22	-81.31 (15)
C14—Fe1—C12—C11	82.46 (13)	C21—Fe1—C23—C22	-37.58 (14)
C13—Fe1—C12—C11	119.47 (18)	C14—Fe1—C23—C22	167.44 (14)
C11—C12—C13—C14	-0.1 (2)	C13—Fe1—C23—C22	126.56 (14)
Fe1—C12—C13—C14	58.60 (15)	C22—C23—C24—C25	-0.3 (3)
C11—C12—C13—Fe1	-58.73 (15)	Fe1—C23—C24—C25	-59.84 (16)
C11—Fe1—C13—C12	37.81 (12)	C22—C23—C24—Fe1	59.52 (16)
C15—Fe1—C13—C12	82.67 (13)	C11—Fe1—C24—C25	-41.6 (4)
C24—Fe1—C13—C12	-157.47 (13)	C15—Fe1—C24—C25	-74.01 (17)
C23—Fe1—C13—C12	-114.53 (13)	C12—Fe1—C24—C25	169.21 (18)
C25—Fe1—C13—C12	168.06 (19)	C23—Fe1—C24—C25	119.1 (2)
C22—Fe1—C13—C12	-73.63 (16)	C22—Fe1—C24—C25	81.40 (15)
C21—Fe1—C13—C12	-41.3 (4)	C21—Fe1—C24—C25	37.62 (14)
C14—Fe1—C13—C12	120.23 (18)	C14—Fe1—C24—C25	-115.04 (15)
C11—Fe1—C13—C14	-82.42 (13)	C13—Fe1—C24—C25	-157.23 (14)
C15—Fe1—C13—C14	-37.56 (12)	C11—Fe1—C24—C23	-160.7 (3)
C24—Fe1—C13—C14	82.30 (15)	C15—Fe1—C24—C23	166.86 (13)
C12—Fe1—C13—C14	-120.23 (18)	C12—Fe1—C24—C23	50.1 (3)
C23—Fe1—C13—C14	125.24 (13)	C25—Fe1—C24—C23	-119.1 (2)
C25—Fe1—C13—C14	47.8 (3)	C22—Fe1—C24—C23	-37.74 (14)
C22—Fe1—C13—C14	166.14 (13)	C21—Fe1—C24—C23	-81.52 (15)
C21—Fe1—C13—C14	-161.6 (3)	C14—Fe1—C24—C23	125.82 (14)
C12—C13—C14—C15	0.0 (3)	C13—Fe1—C24—C23	83.63 (15)
Fe1—C13—C14—C15	58.33 (15)	C23—C24—C25—C21	0.3 (3)
C12—C13—C14—Fe1	-58.36 (15)	Fe1—C24—C25—C21	-59.50 (16)
C11—Fe1—C14—C13	81.02 (13)	C23—C24—C25—Fe1	59.80 (16)
C15—Fe1—C14—C13	119.66 (18)	C22—C21—C25—C24	-0.2 (3)
C24—Fe1—C14—C13	-115.19 (14)	Fe1—C21—C25—C24	59.11 (16)
C12—Fe1—C14—C13	36.95 (12)	C22—C21—C25—Fe1	-59.29 (16)
C23—Fe1—C14—C13	-74.26 (16)	C11—Fe1—C25—C24	166.99 (13)
C25—Fe1—C14—C13	-157.76 (13)	C15—Fe1—C25—C24	125.20 (14)
C22—Fe1—C14—C13	-43.6 (4)	C12—Fe1—C25—C24	-161.4 (3)
C21—Fe1—C14—C13	169.00 (19)	C23—Fe1—C25—C24	-37.78 (14)
C11—Fe1—C14—C15	-38.63 (13)	C22—Fe1—C25—C24	-81.60 (15)
C24—Fe1—C14—C15	125.16 (13)	C21—Fe1—C25—C24	-119.2 (2)
C12—Fe1—C14—C15	-82.70 (13)	C14—Fe1—C25—C24	82.60 (16)
C23—Fe1—C14—C15	166.08 (13)	C13—Fe1—C25—C24	49.3 (3)
C25—Fe1—C14—C15	82.58 (15)	C11—Fe1—C25—C21	-73.81 (17)
C22—Fe1—C14—C15	-163.2 (3)	C15—Fe1—C25—C21	-115.60 (15)
C21—Fe1—C14—C15	49.3 (2)	C24—Fe1—C25—C21	119.2 (2)
C13—Fe1—C14—C15	-119.66 (18)	C12—Fe1—C25—C21	-42.2 (4)
C13—C14—C15—C11	0.2 (2)	C23—Fe1—C25—C21	81.41 (15)
Fe1—C14—C15—C11	59.46 (15)	C22—Fe1—C25—C21	37.59 (14)
C13—C14—C15—Fe1	-59.27 (15)	C14—Fe1—C25—C21	-158.21 (14)
C12—C11—C15—C14	-0.3 (2)	C13—Fe1—C25—C21	168.44 (19)
C1—C11—C15—C14	-174.9 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O2	0.80 (2)	2.08 (2)	2.727 (2)	137 (2)
C5—H5 \cdots O2 ⁱ	0.95	2.53	3.442 (3)	161
C7—H7C \cdots S1 ⁱⁱ	0.98	2.89	3.682 (3)	139

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