

Ferrocene compounds. XXX. Methyl 1'-acetamido-ferrocene-1-carboxylate

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Key indicators

Single-crystal X-ray study

T = 200 K

Mean $\sigma(C-C) = 0.002 \text{ \AA}$

R factor = 0.022

wR factor = 0.057

Data-to-parameter ratio = 15.6

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

The main structural feature of the title compound, $[\text{Fe}(\text{C}_7\text{H}_8\text{NO})(\text{C}_7\text{H}_7\text{O}_2)]$, is the existence of the strong intermolecular hydrogen bond of the $\text{N}-\text{H} \cdots \text{O}=\text{C}$ type between the amide $\text{N}-\text{H}$ group and the carbonyl O atom of the COOCH_3 group from an adjacent molecule [$2.934(2) \text{ \AA}$]. The acetamide O atom participates as a double proton acceptor in intermolecular hydrogen bonds of type $\text{C}-\text{H} \cdots \text{O}$ [$3.411(2)$ and $3.506(2) \text{ \AA}$], thus forming a three-dimensional network. The cyclopentadienyl rings, which are parallel to each other within $1.04(9)^\circ$, are twisted from the eclipsed conformation by only $3.92(1)^\circ$ (maximum). The acetamido, NHCOCH_3 , and ester, COOCH_3 , groups are not in the plane of the cyclopentadienyl rings to which they are attached [dihedral angles are $14.55(10)$ and $7.64(9)^\circ$, respectively]. The deviation from coplanarity is attributed to the intermolecular hydrogen bonds.

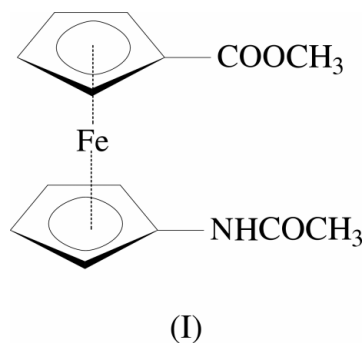
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Comment

Metallocenes and their derivatives are hydrophobic, neutral compounds soluble in organic solvents. They can easily cross cellular membranes and, as a result of these properties, can provide therapeutic and investigation functions in biochemistry, microbiology and medicine (Dombrowski *et al.*, 1986; Ferle-Vidović *et al.*, 2000). The conformational flexibility and the redox properties of ferrocene complexes play important roles in their various applications. Metal-containing polymeric materials with cyclopentadienyl moieties are very attractive materials for electronic, magnetic and optical uses (Okamura *et al.*, 1998). The electronic properties of ferrocene derivatives are considerably influenced by the presence of different functional groups on the cyclopentadienyl (Cp) rings (acyl, carboxylic derived functional groups *etc.*) leading to potentially different applications of these complexes (Oberhoff *et al.*, 1996).



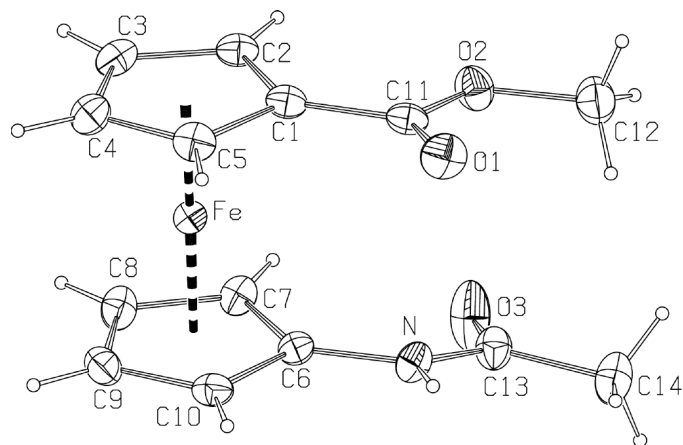


Figure 1
 PLATON (Spek, 1990) drawing with the atom-numbering scheme. The displacement ellipsoids of the non-H atoms are at the 50% probability level.

ferrocene compounds (Lisac & Rapić, 1996; Kovač *et al.*, 1997; Lisac *et al.*, 1997; Kovač *et al.*, 1999; Lapić & Rapić, 2000; Pavlović *et al.*, 2000). A survey of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) lists only two examples of structurally characterized ferrocene compounds functionalized by the acetamido group, namely the mononuclear $\text{Fe}(\text{C}_5\text{H}_4\text{NHCOC}_5\text{H}_4)_2$ and the dinuclear $(\text{CH}_3\text{CONHC}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4\text{CONHC}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4\text{CONHC}_5\text{H}_4)$ (Okamura *et al.*, 1998). The main stereochemical features of these two complexes are the coplanarity of the amido groups and Cp rings and very short intermolecular $\text{N}\cdots\text{O}$ hydrogen bonds in the range 2.74 (2)–2.90 (2) Å. The molecules are joined into polypeptide infinite chains by $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds. This is not the case with the title compound, since the previously mentioned ferrocene derivatives contain two N–H proton-donor and two C=O proton-acceptor groups per molecule in contrast to the one N–H and one C=O group per molecule in the title compound. To the best of our knowledge, this is the first example of a 1,1'-difunctionalized ferrocene containing NHCOC_5H_4 and COOC_5H_4 groups.

The orientation of the cyclopentadienyl rings (Cp) deviates slightly from the ferrocene eclipsed conformation (Fig. 1). The rotation defined by the torsion angle $\text{C}(\text{any Cp atom in ring 1})-\text{Cg1}-\text{Cg2}-\text{C}(\text{any Cp atom in ring 2})$ is in the range 3.84 (1)–3.92 (1)°. The non-H atoms of the NHCOC_5H_4 group lie in a plane with the largest displacement being 0.007 (2) Å for atom C13. Similarly, the non-H atoms of the COOC_5H_4 group are coplanar, with O2 being displaced by 0.007 (1) Å from that plane. The dihedral angle between the plane defined by the non-H atoms of the NHCOC_5H_4 group and the cyclopentadienyl ring to which it is attached is 14.55 (10)°. The dihedral angle between the plane of the COOC_5H_4 group and the attached cyclopentadienyl ring is 7.64 (9)°.

The acetamido $\text{N}-\text{H1N}$ and $\text{C13}=\text{O3}$ groups are *E* oriented with respect to the $\text{N}-\text{C13}$ single bond. The average ring bond distances are 1.4293 (9) and 1.4268 (9) Å for the C1–C5 and C6–C10 rings, respectively. The average C–C ring bond distances for unsubstituted and substituted C atoms

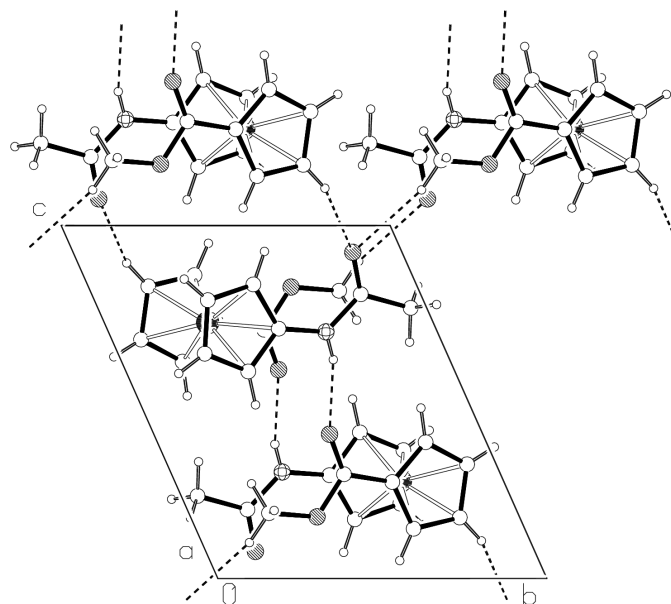


Figure 2
 Packing of the molecules within the unit cell. Hydrogen bonds are indicated by dashed lines.

are given in Table 1. The Fe–C bond distances are in the range 2.0381 (15)–2.0626 (16) Å for the C1–C5 ring and 2.0418 (16)–2.0819 (14) Å for the C6–C10 ring. The Fe–C1 bond distance of 2.0381 (15) Å and Fe–C6 bond of 2.0819 (14) Å are the shortest and longest Fe–C bond distances in the two Cp rings. The value of the average Fe–C bond distance is given in Table 1. The distances from the Fe atom to the ring centroids (Cg) are 1.6503 (2) and 1.6607 (2) Å, respectively, with a $\text{Cg1}-\text{Fe}-\text{Cg2}$ angle of 179.05 (1)°. The acetamido and methylcarboxylate groups are stacked in an ABBA fashion (Fig. 2), enabling centrosymmetrical dimerization by $\text{N}-\text{H}\cdots\text{O}=\text{C}$ intermolecular hydrogen bonds. The dimers are further interconnected by the $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds into a three-dimensional network (Table 2).

Experimental

Methyl 1'-acetamidoferrocene-1-carboxylate was prepared by heating a solution of methyl 1'-azidocarbonylferrocene-1-carboxylate in acetic anhydride at 353 K for 8 h. Work-up of the reaction mixture in the usual manner gave orange crystals (m.p. 381.5–382.0 K), in 42% yield. The structure of the resulting compound was confirmed by elemental analysis, IR, ^1H and ^{13}C NMR spectra (Barišić *et al.*, 2002.). The single crystals were obtained from dichloromethane with *n*-pentane as precipitant.

Crystal data

$[\text{Fe}(\text{C}_7\text{H}_8\text{NO})(\text{C}_7\text{H}_7\text{O}_2)]$
 $M_r = 301.12$
 Triclinic, $P\bar{1}$
 $a = 7.6200$ (1) Å
 $b = 9.5052$ (1) Å
 $c = 10.3956$ (2) Å
 $\alpha = 107.553$ (1)°
 $\beta = 99.684$ (1)°
 $\gamma = 113.209$ (1)°
 $V = 623.39$ (2) Å³

$Z = 2$
 $D_x = 1.604$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2145 reflections
 $\theta = 1-27.5^\circ$
 $\mu = 1.21$ mm⁻¹
 $T = 200$ (2) K
 Irregular prism, orange
 0.42 × 0.38 × 0.21 mm

Data collection

Nonius KappaCCD area-detector diffractometer	2639 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.018$
Absorption correction: none	$\theta_{\text{max}} = 27.4^\circ$
4713 measured reflections	$h = -9 \rightarrow 12$
2772 independent reflections	$k = -12 \rightarrow 13$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.2165P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$
2772 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e } \text{\AA}^{-3}$
178 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C11	1.2118 (16)	N—C6	1.4029 (16)
O2—C11	1.3428 (16)	Fe—C(av)	2.053 (5)
O2—C12	1.4427 (17)	C(Cp)—C(Cp)(av)unsubst.	1.425 (1)
O3—C13	1.2189 (17)	C(Cp)—C(Cp)(av)subst.	1.432 (4)
N—C13	1.3626 (17)		
C1—Fe—C9	156.53 (6)	C1—Fe—C10	121.39 (5)
C1—Fe—C8	161.37 (6)	C2—Fe—C10	156.76 (6)
C9—Fe—C5	120.76 (5)	C11—O2—C12	116.11 (11)
C8—Fe—C5	155.66 (6)	C13—N—C6	125.09 (11)
C9—Fe—C2	160.83 (6)	C13—N—H1N	119.6 (13)
C8—Fe—C2	123.70 (5)	C6—N—H1N	115.0 (13)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N—H1N \cdots O1 ⁱ	0.82 (2)	2.14 (2)	2.934 (2)	164 (1)
C3—H3 \cdots O3 ⁱⁱ	0.93	2.54	3.411 (2)	156
C12—H12B \cdots O3 ⁱⁱⁱ	0.96	2.57	3.506 (2)	166

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 2-z$; (iii) $1-x, 2-y, 2-z$.

Diffraction data were collected on a Nonius KappaCCD diffractometer (capillary optics) at 200 K. 385 frames were collected at a crystal-detector distance of 35 mm, 10 s $^\circ$, 8 sets of ω scans, 1 $^\circ$ per frame. The program *DENZO-SMN* was used for data reduction (Otwinowski & Minor, 1997). No absorption correction has been applied, only scaling. All H atoms were included in calculated posi-

tions as riding atoms, with *SHELXL97* (Sheldrick, 1997) default parameters, except for atom H1N. This was found in a difference Fourier map at a distance from N of 0.82 (2) \AA and refined freely.

Cell refinement: *DENZO* and *COLLECT* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

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