

Acta Crystallographica Section C

**Crystal Structure
Communications**

ISSN 0108-2701

Editor: **George Ferguson**

Methyl 4-(1'-carboxyferrocen-1-yl)butyrate

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Methyl 4-(1'-carboxyferrocen-1-yl)-
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Received 12 October 2006

Accepted 24 October 2006

Online 22 November 2006

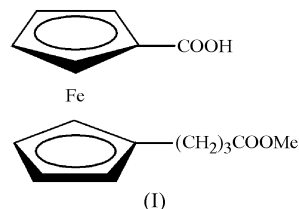
The title compound, [Fe(C₆H₅O₂)(C₁₀H₁₃O₂)], contains a heteroannularly substituted ferrocene unit, with the two substituents, *viz.* 3-(methoxycarbonyl)propyl and carboxyl, both capable of forming O—H···O hydrogen bonds. The keto ester group is stereochemically hindered by the trimethylene spacer and does not participate in intramolecular hydrogen-bond formation. Instead, the carboxy groups form self-complementary intermolecular hydrogen bonds [O···O = 2.650 (2) Å], which join the molecules into centrosymmetric dimers with a graph-set descriptor $R_2^2(8)$.

Comment

In previous reports, we described the synthesis and structural properties of 1'-aminoferrocene-1-carboxylic acid (Fca; H₂NCPeCpCOOH; Pavlović *et al.*, 2002, 2003; Barišić *et al.*, 2002). Fca was successfully coupled with natural amino acids and peptides, giving oligopeptides with antiparallel peptide strands (Barišić *et al.*, 2004, 2006). Unlike all previous metallocene turn structures, these compounds are the first truly organometallic turn mimetics. It was shown that intramolecular hydrogen bonding between podand peptide chains introduced helical conformations of the metallocene. We planned to research the influence of a trimethylene spacer between a carboxylic acid or amine group and a ferrocene unit on the formation of intramolecular hydrogen bonds. For that purpose, N-protected derivatives of 1'-(3-aminopropyl)-ferrocene-1-carboxylic acid, H₂N(CH₂)₃CpFeCpCOOH, and 1'-amino-1-ferrocenebutyric acid, H₂NCPeCp(CH₂)₃COOH, were synthesized (Barišić *et al.*, 2003). The crystal structure analysis of both compounds confirmed only intermolecular hydrogen bonds. In this context, the crystal structure of the intermediate 'ester-acid' (I) is presented.

Within the ferrocenyl group in (I) (Fig. 1), the Fe—C bond distance range for the unsubstituted C atoms is 2.038 (2)–2.063 (2) Å, and the bonds to the substituted C atoms have

values that do not deviate significantly from that range. The cyclopentadienyl (Cp) rings are almost eclipsed. The dihedral angle between the C1/Cg1/Fe1/Cg2 and C7/Cg2/Fe1/Cg1 planes is 2.34 (16)° (Cg1 and Cg2 are the centroids of the C1–C5 and C7–C11 rings, respectively). The Fe-to-centroid



distances are 1.6487 (10) (Cg1) and 1.6561 (10) Å (Cg2), and the Cg1—Fe1—Cg2 angle is 179.46 (2)°. The exocyclic C1—C6 bond distance [1.458 (3) Å] is slightly shortened owing to the coupling of the Cp ring π -electrons and the carboxyl group. While this distance is in agreement with the theoretical C_{ring}—C_{COOH} bond distance of 1.460 Å (Lin *et al.*, 1998), indicating π -electron delocalization between the carboxyl group and the Cp ring, the C7—C12 bond [1.496 (3) Å] is slightly longer, but still shorter than both C12—C13 [1.525 (3) Å] and C13—C14 [1.523 (3) Å] of the trimethylene spacer, which are predominantly σ in character. The double-bond character of the C15=O3 bond is reflected in its length, as is the single-bond character of C15—O4 (Table 1). In contrast, the carboxyl group geometry for the C6—O1 and C6—O2 bonds (Table 1) is consistent with disorder between the single and double C—O bonds (see below), with the C6—O1 bond being slightly longer (Allen *et al.*, 1987). The deviation of the carboxyl group from coplanarity with the C1—C5 Cp ring is not significant [the dihedral angle is 3.03 (3)°].

Neighboring molecules are joined into discrete centrosymmetric dimers (Fig. 2) *via* O—H···O intermolecular hydrogen bonding (Table 2) [$R_2^2(8)$ according to graph-set analysis], which is the most frequent supramolecular synthon in molecular fragments containing carboxyl groups. The same synthon is found in the structure of 1,1'-ferrocenedicarboxylic acid (at 78 K; Takusagawa & Koetzle, 1979), with O···O distances in the range 2.5997 (1)–2.6597 (1) Å; in the structure of ferrocenecarboxylic acid (Cotton & Reid, 1985), with

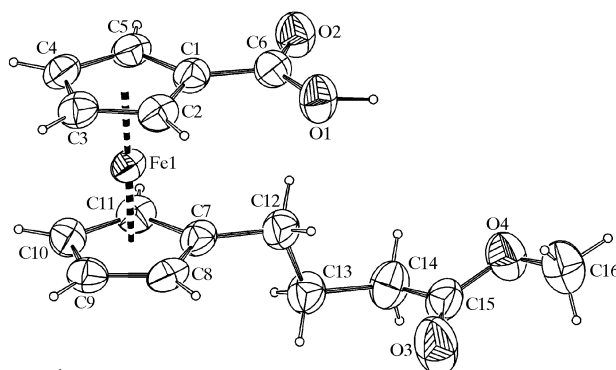


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Only the major component (65%) of the disordered H atom of the carboxyl group is shown.

O···O distances of 2.714 (14) Å; and in the structure of 1'-(*tert*-butoxycarbonylamino)ferrocene-1-carboxylic acid [2.656 (3) and 2.663 (3) Å for two independent molecules; Pavlović *et al.*, 2002]. There are no important contacts between the dimers, other than van der Waals contacts.

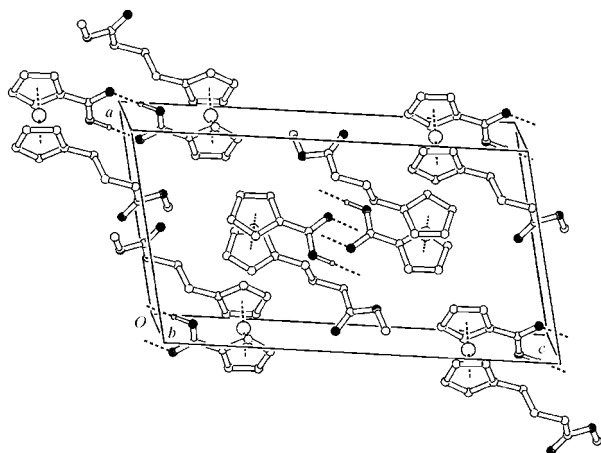


Figure 2

A view of the crystal structure of (I). Dimerization occurs with eight-membered ring formation *via* intermolecular hydrogen bonds (dashed lines). Only the major component (65%) of the disordered H atom of the carboxyl group is shown; other H atoms have been omitted for clarity.

Experimental

Compound (I) was prepared by partial esterification of 1'-carboxyferrocene-1-ylbutyric acid, which was obtained in five steps starting from *N,N*-diphenylferrocenecarboxamide (Barišić *et al.*, 2003). Work-up of the reaction mixture gave orange crystals (m.p. 342–348 K) in 94% yield.

Crystal data

[Fe(C₆H₅O₂)(C₁₀H₁₃O₂)]
M_r = 330.15
 Monoclinic, *P*2₁/*n*
a = 10.4324 (8) Å
b = 7.5565 (5) Å
c = 18.9837 (15) Å
 β = 102.641 (7)°
V = 1460.26 (19) Å³

Z = 4
D_x = 1.502 Mg m⁻³
 Mo *K*α radiation
 μ = 1.05 mm⁻¹
T = 296 (2) K
 Plate, orange
 0.56 × 0.50 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer with a Sapphire-3 CCD detector
 φ and ω scans
 Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2004)
T_{min} = 0.461, *T_{max}* = 0.881

30324 measured reflections
 3174 independent reflections
 3120 reflections with *I* > 2σ(*I*)
R_{int} = 0.042
 θ_{\max} = 27.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.041
wR (*F*²) = 0.090
S = 1.14
 3174 reflections
 191 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.948P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{Å}^{-3}$

C-bound H atoms were positioned geometrically and refined as riding, with *U_{iso}*(H) = 1.2 or 1.5 times *U_{eq}*(C). Two possible positions

Table 1

Selected bond lengths (Å).

O1—C6	1.282 (3)	O4—C15	1.334 (3)
O2—C6	1.260 (3)	O4—C16	1.431 (4)
O3—C15	1.195 (3)		

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>
O1—H1A···O2 ⁱ	1.00	1.65	2.650 (3)	176
O2—H2A···O1 ⁱ	0.85	1.80	2.650 (3)	180

Symmetry code: (i) $-x + 2, -y + 1, -z$.

of the H atom of the carboxyl group at C6 were found in a difference Fourier map at the final stages of the refinement, with O1—H1 and O2—H2A bond distances of 1.00 and 0.85 Å, respectively. This is consistent with the apparent C6—O1 and C6—O2 bond distances being disordered with each other. The occupancy factors were estimated only from the electron densities found in the difference map and were fixed, thus yielding 65:35 H-atom positional disorder, with the major component attached to O1 and the minor component attached to O2. The coordinates of the partially occupied H-atom sites were fixed in the final refinement, yielding the hydrogen-bond geometry reflected in Table 2. The *U_{iso}* values of these H atoms were set at 1.2*U_{eq}*(O).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON98* (Spek, 1998).

This research was supported by the Ministry of Science and Technology of the Republic of Croatia (grant Nos. 0119633 and 0058023).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3052). Services for accessing these data are described at the back of the journal.

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