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## Key indicators

Single-crystal X-ray study  
 $T = 150\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.034  
 $wR$  factor = 0.087  
Data-to-parameter ratio = 17.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**(*S,S*<sub>p</sub>)-2-[4-(1-Methylethyl)-4,5-dihydro-oxazol-1-yl]ferrocenecarboxylic acid**

Chiral oxazolinyl-modified ferrocenecarboxylic acid, (*S,S*<sub>p</sub>)-[Fe{ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>(CO<sub>2</sub>H-1)(C<sub>6</sub>H<sub>10</sub>NO-2)}( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] or [Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>12</sub>H<sub>14</sub>NO<sub>3</sub>)], crystallizes as a molecular compound, featuring an intramolecular O—H···N hydrogen bond between the carboxyl hydroxy group and oxazoline N atom, with an O···N separation of 2.559 (3) Å. The ferrocene substituents are rotated only slightly from the plane of their parent cyclopentadienyl ring: 7.65 (17) (oxazoline) and 2.3 (3)<sup>o</sup> (carboxyl).

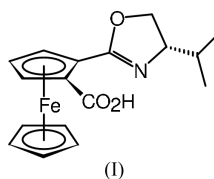
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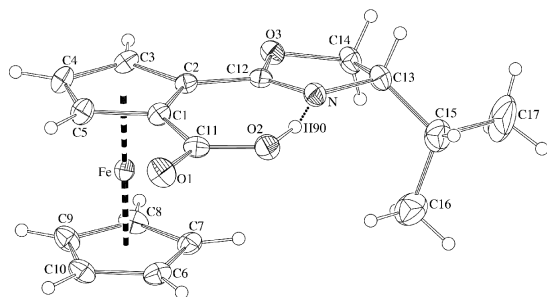
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## Comment

Ferrocene dihydrooxazoles (or oxazolines) modified with other donor groups have recently attracted considerable scientific interest due to their efficiency and versatility as ligands in enantioselective catalysis. They have also been used as precursors for the preparation of other chiral ferrocene derivatives (Sutcliffe & Bryce, 2003). Since this synthetic utility relies on the availability of suitable, mostly polar, derivatives, there is still a demand for substituted ferrocenyl-oxazolines. Those modified with a carboxy group at the ferrocene unit are so far represented only by (*S,S*<sub>p</sub>)-2-[4-(2-methylprop-2-yl)-4,5-dihydrooxazol-1-yl]ferrocenecarboxylic acid (Ahn *et al.*, 1996) and (*S,S*<sub>p</sub>)-2-[4-(1-methylethyl)-4,5-dihydrooxazol-1-yl]-3-trimethylsilylferrocenecarboxylic acid (Bolm & Kuhn, 2002). However, neither of these acids was structurally characterized. This contribution deals with the synthesis and structure of another carboxyferrocene oxazoline, namely (*S,S*<sub>p</sub>)-2-[4-(1-methylethyl)-4,5-dihydrooxazol-1-yl]ferrocenecarboxylic acid, (I).



The title compound was synthesized by diastereoselective *ortho*-metallation of (*S*)-2-[4-(1-methylethyl)-4,5-dihydrooxazol-1-yl]ferrocene (Richards & Mulvaney, 1996) followed by quenching of the lithio intermediate with carbon dioxide and subsequent acidification. The acid was obtained as an air-stable rust-brown crystalline solid after recrystallization from ethyl acetate–hexane and characterized by the standard spectroscopic methods and elemental analysis. Notably, the <sup>1</sup>H NMR spectrum features a broad singlet at  $\delta_{\text{H}} -0.59$  due to the carboxyl H atom, indicating that hydrogen bonding observed in the solid state (see below) is likely retained, even in CDCl<sub>3</sub> solutions.



**Figure 1**  
A view of the molecular structure of (I), showing the atom-labelling scheme and the O—H...N hydrogen bond as a dashed line. Displacement ellipsoids are drawn at the 30% probability level.

The molecular structure of the acid is shown in Fig. 1 and the relevant bond lengths and angles are given in Table 1. The molecule is chiral, having the (*S,S<sub>p</sub>*) configuration, as expected from the known course of the metallation reaction (Richards & Mulvaney, 1996). Its configuration is implied by the reference chiral centre at the oxazoline unit inherent in natural (*S*)-valinol and further corroborated by the enantiomorph parameter (Flack, 1983).

As far as bond lengths and angles are concerned, the molecular geometry compares favourably with other ferrocene oxazolines, *e.g.* 1-(diphenylphosphanyl)-3-methyl-2-[4-(1-methylethyl)-4,5-dihydrooxazol-1-yl]ferrocene and 1-phenylseleno-2-[4-(1-methylethyl)-4,5-dihydrooxazol-1-yl]ferrocene (Nishibayashi *et al.*, 1997), and with ferrocene acids, *e.g.* ferrocenecarboxylic acid (Lin *et al.*, 1998), 1,1'-ferrocenedicarboxylic acid (Takusagawa & Koetzle, 1979) and 1'-(diphenylphosphanyl)ferrocenecarboxylic acid (Podlaha *et al.*, 1995).

The ferrocene framework has a regular arrangement and shows only a negligible tilt [1.64 (17)°] of the cyclopentadienyl rings [*cf.* the Cg1—Fe—Cg2 angle of 179.52 (7)°; Cg1 and Cg2 are the centroids of the C1—C5 and C6—C10 cyclopentadienyl rings, respectively]. The respective Fe—Cg distances are 1.6392 (13) (Cg1) and 1.6501 (13) Å (Cg2). The slightly shorter (by only *ca* 0.7%) distance to the substituted ring (C1—C5) likely reflects an electron-acceptor nature of the substituents, resulting in an enhanced bonding due to an electron-density transfer towards this ring.

The oxazoline ring is almost perfectly planar, with a maximum deviation from the mean ring plane of 0.078 (3) Å for C14. The oxazoline substituent and the carboxyl group are nearly coplanar with their parent cyclopentadienyl ring; the dihedral angles of the least-squares planes are 2.3 (3)° for the carboxyl group and 7.65 (17)° for the oxazoline ring. Such an arrangement permits extensive electronic conjugation and is further aided by intramolecular O—H...N hydrogen bonding between the carboxyl hydroxy group and oxazoline N atom (Table 2). This interaction results in the formation of a planar ring of six non-H atoms and is the most important interaction of the individual molecular parts. The 'true' intermolecular interactions involve only weak C—H...X hydrogen bonds without significant contributions from C—H... $\pi$ -ring and  $\pi$ - $\pi$  interactions. Apparently, the crystal packing is influenced by

the presence of the polar oxazoliny group, since it is very different from the above-mentioned ferrocenecarboxylic acids, whose crystal structures are typically built up from dimers joined by double hydrogen bridges between the carboxyl groups.

Like other ferrocenecarboxylic acids (Zakaria *et al.*, 2001; Braga *et al.*, 2003), the title compound could possibly serve as a building block for the preparation of self-assembled organometallic solid materials (hydrogen bonded and/or ionic) with a defined chirality. Further research in this area is currently underway.

## Experimental

(*S*)-2-[4-(1-Methylethyl)-4,5-dihydrooxazol-1-yl]ferrocene (0.297 g, 1.0 mmol; Richards & Mulvaney, 1996) was dissolved, under argon, in anhydrous diethyl ether (15 ml) and *N,N,N',N'*-tetramethyl-1,2-diaminoethane (0.20 ml, 1.3 mmol) was added. The solution was cooled to 198 K (ethanol—CO<sub>2</sub>), butyllithium (0.6 ml, 2.5 *M* in hexanes, 1.5 mmol) was slowly introduced, and the reaction mixture was stirred for 2 h at 198 K and then at room temperature for 5 min. Solid CO<sub>2</sub> (*ca* 10 g, excess) was added, whereupon a yellow precipitate formed. After stirring for another 30 min at room temperature, the mixture was extracted into aqueous 5% KOH (20 ml). The extract was acidified with 40% H<sub>3</sub>PO<sub>4</sub>, saturated with NaCl and extracted into dichloromethane (several times). The combined organic phase was washed with brine, dried (MgSO<sub>4</sub>) and evaporated. The dark residue was purified by flash chromatography on silica gel (dichloromethane—methanol, 10:1 *v/v*), the orange eluate was evaporated and the residue recrystallized from ethyl acetate—hexane (yield: 148 mg, 43%) as rust-brown needles. NMR (CDCl<sub>3</sub>):  $\delta_{\text{H}}$  -0.59 (*s*, 1H, CO<sub>2</sub>H), 1.05, 1.09 (2  $\times$  *d*, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, 3H, Me of CHMe<sub>2</sub>); 1.86 (*d of sept*, <sup>3</sup>*J*<sub>HH,1</sub>  $\sim$  <sup>3</sup>*J*<sub>HH,2</sub>  $\sim$  6.7 Hz, 1H, CH of CHMe<sub>2</sub>), 4.07 (*ddd*, *J*<sub>HH</sub> = 6.5, 7.7 and 9.7 Hz, 1H, CH<sup>ox</sup>), 4.25–4.31 (*m*, 1H, CH<sub>2</sub><sup>ox</sup>; obscured by the strong C<sub>5</sub>H<sub>5</sub> signal), 4.29 (*s*, 5H, C<sub>5</sub>H<sub>5</sub>), 4.52 (*dd*, *J*<sub>HH</sub> = 8.7, 9.7 Hz, 1H, CH<sub>2</sub><sup>ox</sup>), 4.64 (apparent *t*, *J*<sub>HH</sub> = 2.7 Hz, 1H, C<sub>5</sub>H<sub>3</sub>), 4.89, 5.34 (2  $\times$  *dd*, *J*<sub>HH</sub> = 1.7 and 2.7 Hz, 1H, C<sub>5</sub>H<sub>3</sub>);  $\delta_{\text{C}}$  18.41, 18.81 (Me of CHMe<sub>2</sub>), 32.61 (CH of CHMe<sub>2</sub>), 66.05 (*C*<sub>ipso</sub> of C<sub>5</sub>H<sub>3</sub>), 70.34 (CH<sup>ox</sup>), 71.80 (C<sub>5</sub>H<sub>5</sub>), 71.85 (CH<sub>2</sub><sup>ox</sup>), 72.35 (CH of C<sub>5</sub>H<sub>3</sub>), 72.93 (*C*<sub>ipso</sub> of C<sub>5</sub>H<sub>3</sub>), 73.51, 77.12 (2  $\times$  CH of C<sub>5</sub>H<sub>3</sub>), 170.03, 171.13 (C=N and CO<sub>2</sub>H). IR (Nujol): 1704 (*s*), 1658 (*s*,  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=N}}$ ), 1297 (*s*), 1287 (*s*), 1260 (*s*), 1173 (*s*), 1151 (*s*), 1143 (*m*), 1110 (*m*), 1068 (*m*), 1041 (*s*), 994 (*s*), 935 (*s*), 779 (*s*), 546 (*s*) cm<sup>-1</sup>. Analysis calculated for C<sub>17</sub>H<sub>19</sub>FeNO<sub>3</sub>: C 59.85, H 5.61, N 4.11%; found: C 59.74, H 5.79, N 4.00%.

### Crystal data

[Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>12</sub>H<sub>14</sub>NO<sub>3</sub>)]  
*M<sub>r</sub>* = 341.18  
Tetragonal, *P*4<sub>3</sub>  
*a* = 11.4599 (2) Å  
*c* = 11.6864 (2) Å  
*V* = 1534.77 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.477 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation  
Cell parameters from 1852 reflections  
 $\theta$  = 1.0–27.5°  
 $\mu$  = 0.99 mm<sup>-1</sup>  
*T* = 150 (2) K  
Prism, brown  
0.52  $\times$  0.40  $\times$  0.28 mm

### Data collection

Nonius KappaCCD diffractometer  
 $\omega$  and  $\varphi$  scans  
Absorption correction: multi-scan (SORTAV; Blessing, 1997)  
*T*<sub>min</sub> = 0.681, *T*<sub>max</sub> = 0.757  
27433 measured reflections  
3497 independent reflections

3323 reflections with *I* > 2 $\sigma$ (*I*)  
*R*<sub>int</sub> = 0.044  
 $\theta$ <sub>max</sub> = 27.5°  
*h* = -14  $\rightarrow$  14  
*k* = -14  $\rightarrow$  14  
*l* = -14  $\rightarrow$  15

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.8632P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.087$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.04$	$\Delta\rho_{\max} = 0.71 \text{ e } \text{\AA}^{-3}$
3497 reflections	$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$
205 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	1652 Friedel pairs
	Flack parameter = $-0.020$ (17)

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

N—C12	1.269 (3)	C1—C11	1.500 (4)
N—C13	1.477 (4)	C2—C12	1.461 (4)
O1—C11	1.213 (3)	C13—C15	1.527 (5)
O2—C11	1.317 (4)	C13—C14	1.536 (4)
O3—C12	1.349 (3)	C15—C16	1.493 (6)
O3—C14	1.473 (3)	C15—C17	1.528 (6)
C12—N—C13	108.1 (2)	N—C13—C14	102.9 (2)
C12—O3—C14	105.1 (2)	C15—C13—C14	120.6 (3)
O1—C11—O2	120.6 (3)	C16—C15—C13	112.5 (4)
N—C12—O3	118.1 (2)	C16—C15—C17	108.9 (4)
N—C13—C15	111.7 (3)	C13—C15—C17	109.6 (3)
C11—C1—C2—C12	2.5 (4)		

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H90 $\cdots$ N	0.98 (7)	1.61 (6)	2.558 (3)	161 (6)
C3—H3 $\cdots$ O3 <sup>i</sup>	0.93	2.54	3.427 (3)	160
C8—H8 $\cdots$ N <sup>i</sup>	0.93	2.58	3.470 (3)	159

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

H atoms, except for carboxyl atom H90 which was identified in a difference electron-density map and isotropically refined [ $O2-H90 = 0.99$  (6)  $\text{\AA}$  and  $C11-O2-H90 = 120$  (4) $^\circ$ ], were included in calculated positions, with C—H = 0.96 (methyl), 0.97 (methylene), 0.98 (methine) and 0.93  $\text{\AA}$  (aromatic), and assigned  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  (aromatic, methine and methylene) or  $1.5U_{\text{eq}}(\text{C})$  (methyl). The

peripheral isopropyl substituent shows a slight disorder, resulting in larger anisotropic displacement parameters of its C atoms (particularly C17) compared with the rest of the molecule and, consequently, the space occupied by this group accommodates the largest residual electron density. Attempted refinement of the isopropyl group over two positions failed.

Data collection: COLLECT (Nonius, 1997–2000); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2001).

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