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Synthesis and Crystal Structure of Methyl-2-hydroxy ferrocenyl methyl acrylate

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Abstract : The crystal structure of the title compound has been determined by means of X-Ray diffraction. The compound crystallizes in the tetragonal space group I -4 with $a = 20.6133(4) \text{ \AA}$, $b = 20.6133(4) \text{ \AA}$, $c = 6.2168(2) \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. The small dihedral angle of $2.96 (11)^\circ$ between the unsubstituted and substituted Cp rings exposes that the two Cp rings are parallel to each other. The molecular structure of the compound is stabilized by weak intramolecular C-H...O type of hydrogen bond. The crystal packing is controlled by weak intermolecular O-H...O, C-H... π and π - π interactions. The interactions C11-H11...O2 and C13-H13A...O3 generates a five-membered ring, with S(5) graph-set-motif and the interaction C6-H6...O2 generates a nine-membered ring, with S(9) graph-set-motif. The C6-H6...O2 and C11-H11...O2 interactions together constitute a pair of bifurcated acceptor bonds generating a ring of graph set $R_2^1(8)$.

Keywords: Single-crystal X-ray study, Ferrocene, Weak interaction, R factor = 0.028.

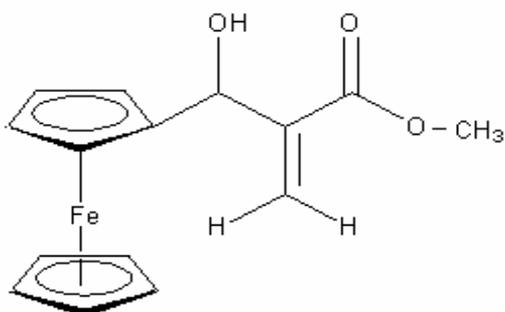
Introduction

Ferrocene is an organometallic compound with the formula $\text{Fe}(\text{C}_5\text{H}_5)_2$. It is the prototypical metallocene, a type of organometallic chemical compound consisting of two cyclopentadienyl rings bound on opposite sides of a central metal atom. Such organometallic compounds are also known as sandwich compounds¹. The rapid growth of organometallic chemistry is often attributed to the excitement arising from the discovery of ferrocene and its many analogues. An interest in heterocyclic ferrocene derivatives is due first of all to their unique photophysical², magnetic³, and redox⁴, properties along with the possibility of their application in analytical⁵, and medicinal⁶, chemistry, and as efficient catalytic reagents in asymmetric synthesis⁷. Ferrocene, because of its aromatic character, facilitates several substitution reactions whereby a range of low molecular mass calamitic systems can be prepared by monosubstitution, or, 1,1-, 1,2-, 1,3-disubstitution or 1,1,3-trisubstitution of the ferrocene nucleus⁸. Derivatives of Ferrocene exhibit a variety of medicinal properties by serving as antibacterial, antimalarial and antitumor agents⁹. Azalactone ferrocene (AzaFecp) and Thiomorpholide amido methyl ferrocene (ThioFecp) show significant anti-HIV activity at nanomolar concentrations against an Indian isolate of HIV-1_{93IN101} in Sup-T1 cell line¹⁰. In the view of wide

range of pharmacological activities of the Ferrocene derivatives, the X-ray crystallographic studies of the title compound have been undertaken in order to study the molecular conformations in detail.

Experimental

A mixture of ferrocenecarboxaldehyde (1mmol) and methyl acrylate (1.5mmol) was stirred in THF in the presence of DABCO (0.2mmol) till the formation of product as evidenced by TLC analysis. After the reaction, the mixture was quenched with water (100 mL) and aqueous HCl (50 mL). Then the reaction mixture was extracted with CHCl_3 (3×30 mL). The organic layer was dried over anhydrous Na_2SO_4 . The crude mixture was separated by column chromatography using ethyl acetate and hexane as eluent (5:95).



Scheme

X-Ray Structure Determination

Single crystal X-ray diffraction data for the compound at room temperature was collected by Bruker Kappa diffractometer with $\text{Mo K}\alpha$ radiation using $\omega/2\theta$ scan mode. SMART APEX2 CCD area detector with $\text{Mo K}\alpha$ radiation and ω scan mode was applied to obtain an accurate unit cell parameters and orientation matrix within the least-square fit of several high angle reflections in the ranges $2.8^\circ < \theta < 28.30^\circ$. Cell refinement and data reduction were carried out using SAINT. A total of 6572 reflections were collected, resulting in 2183 independent reflections of which 1952 had $I > 2\sigma(I)$. The intensities for Lorentz and polarization effects and absorption corrections were corrected by using SADABS¹¹. The structure of compound was solved by direct method procedure as implemented in SHELXS97¹², program. The full matrix least square refinement using SHELXL97 program was used to include the position of all non hydrogen atoms. The thermal parameters for each atom were assigned a value of 0.05 (U's) in the initial stage and refinement was followed. The initial scale factor was pegged at 1.0. Thereafter the anisotropic refinement for a few cycles of full matrix least square was continued. At this stage the positions of all hydrogen's were geometrically fixed at calculated positions and they were allowed to ride on the corresponding non hydrogen atoms. The minimum and maximum value of residual electron density was $-0.28, 0.199 \text{ e.}\text{\AA}^{-3}$ and the final R-factor was 0.028. Crystallographic data of the compound is summarized in Table 1.

Results and Discussion

Fig. 1 shows the ORTEP plot of the molecule drawn at 30% probability ellipsoid level with atom numbering scheme. Fig 2 shows the packing of compound viewed down 'c' axis. The Fe(1)-Cg(1) and Fe(1)-Cg(2) distances are 1.6495 (3) \AA and 1.6557 (3) \AA , respectively, and the Cg(1)-Fe(1)-Cg(2) angle is 177.46 (3) $^\circ$, where Cg(1) and Cg(2) are the centroids of the substituted and unsubstituted Cyclopentadienyl (Cp) rings, which is comparable to the literature value of Fe-Cg(s) and Fe-Cg(as) distances are 1.6454 (13) \AA and 1.6510 (15) \AA , respectively, and the Cg(s)-Fe-Cg(as) angle is 178.90 (8) $^\circ$ ¹³. The small dihedral angle of 2.96 (11) $^\circ$ between the unsubstituted and substituted Cp rings exposes that the two Cp rings are parallel to each other. Table 2 summarizes the selected geometrical parameters of the compound.

The molecular structure of the compound is stabilized by weak intramolecular C-H...O type of

hydrogen bond. The atom O2 is acting as potent acceptor for C6-H6...O2 and C11-H11...O2 hydrogen bonds in which atoms C6 and C11 donates a proton. The atom O3 is acting as potent acceptor for C13-H13A...O3 hydrogen bond in which atom C13 donates a proton. The crystal packing is stabilized by weak intermolecular O1-H1...O1 (distance of 2.803 (1) Å), C-H... π [C9-H9...Cg2 (distance of 3.734 (3) Å), where Cg2 is the centroid of the ring defined by the atoms C6-C10] and π - π [Cg1...Cg2 (x, y, z) distance of 3.304 (2) Å), where Cg1 and Cg2 are the centroid of the ring defined by the atoms C1-C5 and C6-C10 respectively] interactions. Table 3 gives the Hydrogen bond data of the compound.

The interactions C11-H11...O2 and C13-H13A...O3 generates an S(5) graph set motif and the interaction C6-H6...O2 generates an S(9) graph set motif. The C6-H6...O2 and C11-H11...O2 interactions together constitute a pair of bifurcated acceptor bonds generating a ring of graph set $R_2^1(8)^{14}$.

Conclusions

Derivatives of Ferrocene exhibit a variety of medicinal properties by serving as antibacterial, antimalarial, antitumor agents and Certain ferrocene derivatives based coordination complexes exhibits moderate antifungal activity. In the title compound the small dihedral angle between the unsubstituted and substituted Cp rings shows two Cp rings are parallel to each other. The molecular structure of the compound is stabilized by weak intramolecular C-H...O type of hydrogen bond. The crystal packing is controlled by weak intermolecular O-H...O, C-H... π and π - π interactions. Presence of inter and intra molecular hydrogen bonds in the title compound shows that, the derivative exhibit wide range of biological activities.

Table. 1 Crystal data, data collection and structure refinement

Formula	C15H16FeO3
Formula weight	300.13
Crystal system	Tetragonal
Space group	I -4
T (K)	295(2)
a (Å)	20.6133(4)
b (Å)	20.6133(4)
c (Å)	6.2168(2)
α(°)	90
β(°)	90
γ(°)	90
V (Å³)	2641.6(1)
Z	8
D_x (g cm⁻³)	1.509
F(000)	1248
μ (mm⁻¹)	1.142
Crystal size (mm)	0.20 0.20 0.20
Θ range (°)	2.8–28.30
hkl range	-24 ≤ h ≤ 27 -27 ≤ k ≤ 27 -8 ≤ l ≤ 8
Reflections	
Collected	6572
Unique (R_{int})	2183 (0.028)
With [I>2σ(I)]	1952
Number of parameters	174
R(F) [I>2σ(I)]	0.028
wR(F²) [I>2σ(I)]	0.0672
R(F) [all data]	0.0325
wR(F²) [all data]	0.0672
Goodness of fit	0.98
Max/min $\Delta\rho$ (e Å⁻³)	0.199/-0.28
CCDC NO	848738

Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC-848738. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

Table. 2 Selected geometrical parameters (Å, °) with su's in parentheses

C1-Fe1	2.047(2)	C10-Fe1	2.044(4)
C2-Fe1	2.047(3)	C1-C11	1.513(3)
C3-Fe1	2.045(3)	C11-O1	1.438(3)
C4-Fe1	2.034(2)	C11-C12	1.508(4)
C5-Fe1	2.047(3)	C12-C13	1.326(4)
C6-Fe1	2.028(3)	C12-C14	1.486(3)
C8-Fe1	2.030(3)	C14-O2	1.203(3)
C7-Fe1	2.020(3)	C14-O3	1.331(3)
C9-Fe1	2.042(4)	C15-O3	1.444(3)
C5-C1-Fe1	69.7(1)	C6-Fe1-C8	67.5(1)
C2-C1-Fe1	69.6(1)	C7-Fe1-C4	144.6(2)
C11-C-Fe1	132.7(1)	C6-Fe1-C4	172.1(2)
C3-C2-Fe1	69.6(2)	C8-Fe1-C4	112.5(2)
C1-C2-Fe1	69.7(2)	C7-Fe1-C9	67.2(2)
C4-C3-Fe1	69.4(2)	C6-Fe1-C9	66.3(2)
C2-C3-Fe1	69.7(2)	C8-Fe1-C9	40.0(3)
C3-C4-Fe1	70.3(2)	C4-Fe1-C9	108.3(2)
C5-C4-Fe1	69.9(2)	C7-Fe1-C10	66.8(2)
C1-C5-Fe1	69.7(1)	C6-Fe1-C10	39.24(2)
C4-C5-Fe1	68.9(2)	C8-Fe1-C10	67.0(2)
C10-C6-Fe1	71.0(2)	C4-Fe1-C10	133.0(2)
C7-C6-Fe1	69.7(2)	C9-Fe1-C10	39.4(2)
C9-C8-Fe1	70.5(2)	C7-Fe1-C3	114.8(2)
C7-C8-Fe1	69.2(2)	C6-Fe1-C3	147.6(2)
C6-C7-Fe1	70.3(2)	C8-Fe1-C3	107.5(2)
C8-C7-Fe1	70.0(2)	C4-Fe1-C3	40.3(2)
C10-C9-Fe1	70.4(2)	C9-Fe1-C3	131.4(2)
C8-C9-Fe1	69.6(3)	C10-Fe1-C3	170.3(2)
C6-C10-Fe1	69.7(2)	C7-Fe1-C2	110.6(2)
C9-C10-Fe1	70.2(3)	C6-Fe1-C2	118.1(2)
O1-C11-C12	110.9(2)	C8-Fe1-C2	132.7(3)
O1-C11-C1	109.0(2)	C4-Fe1-C2	68.1(2)
O2-C14-O3	122.6(2)	C9-Fe1-C2	170.9(2)
O2-C14-C12	124.9(2)	C10-Fe1-C2	148.9(2)
O3-C14-C12	112.5(2)	C3-Fe1-C2	40.63(1)
C14-O3-C15	116.4(2)	C7-Fe1-C1	134.8(2)
C7-Fe1-C6	40.0(2)	C6-Fe1-C1	112.5(1)
C7-Fe1-C8	40.7(2)	C8-Fe1-C1	173.0(3)
C4-Fe1-C1	68.6(1)	C8-Fe1-C5	144.4(2)
C9-Fe1-C1	146.9(2)	C4-Fe1-C5	41.1(1)
C10-Fe1-C1	117.7(2)	C9-Fe1-C5	115.0(2)
C3-Fe1-C1	68.5(1)	C10-Fe1-C5	110.9(2)
C2-Fe1-C1	40.7(1)	C3-Fe1-C5	68.4(1)
C7-Fe1-C5	173.9(2)	C2-Fe1-C5	68.2(1)
C6-Fe1-C5	134.7(1)	C1-Fe1-C5	40.5(1)

Table. 3 Non-Bonded interactions and possible hydrogen bonds (Å, °)

D-H...A	D-H	H...A	D...A	DHA
C6-H6...O2	0.93	2.49	3.171(4)	130.6
C11-H11...O2	0.98	2.46	2.879(3)	105.5
C13-H13A...O3	0.93	2.37	2.691(3)	100.1
O1-H1-O1i	0.82	2.03	2.803(1)	158.0
C9-H9...Cg2ii	0.93	2.93	3.734(3)	146.0

Cg2 is centroid of the ring defined by the atoms C6-C10

Symmetry Equivalent position:

(i) $-y, x, -z$ (ii) $-1/2+y, 1/2-x, 1/2-z$

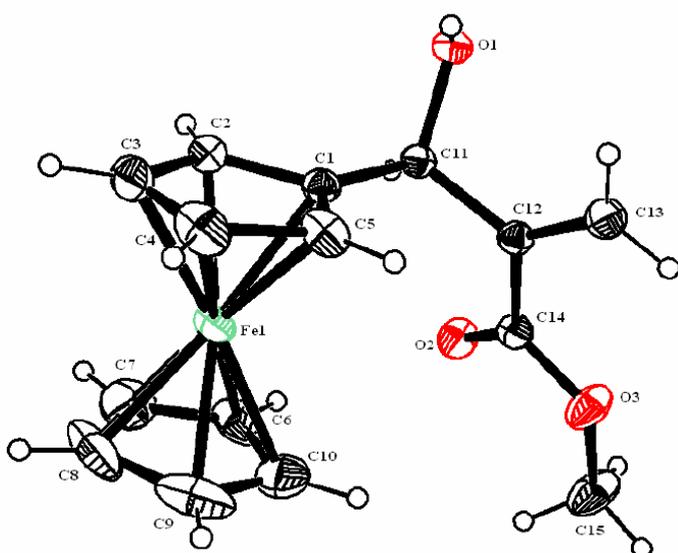


Fig. 1 ORTEP plot of the compound drawn at 30% probability

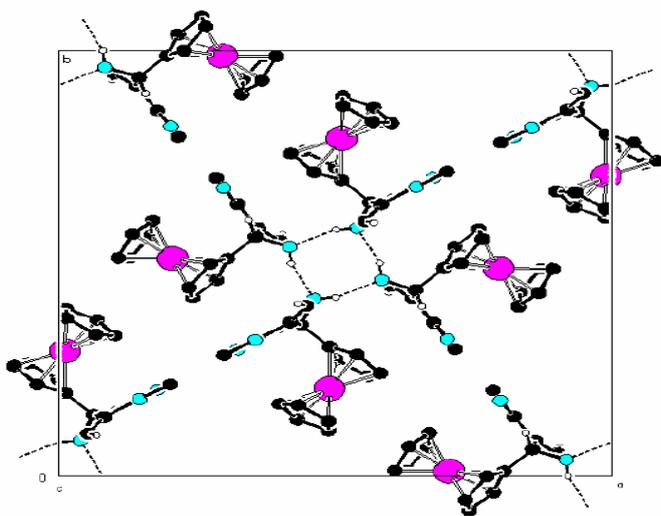


Fig. 2 Packing of the compound viewed down 'c' axis. Hydrogen bonds are shown as dashed lines.

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