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1-Ferrocenyl-9-oxabicyclo[3.3.1]nonan-5-ol*

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Abstract. $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_{17}\text{O}_2)]$, $M_r = 326.2$, orthorhombic, $Pbcn$, $a = 28.833$ (4), $b = 12.207$ (3), $c = 8.4933$ (13) Å, $V = 2990$ (2) Å³, $Z = 8$, $D_x = 1.450$ (1) g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 10.1$ cm⁻¹, $F(000) = 1376$, $T = 299$ K, $R = 0.036$ for 1591 data having $F_o^2 > 3\sigma(F_o^2)$ measured by diffractometer. The molecule exists 100% as the lactol with no detectable concentration of the open form as no carbonyl stretch is observed by IR spectroscopy. The Fe atom lies 1.641 (1) and 1.647 (1) Å from the cyclopentadienyl ring planes, and the Fe–centroid vectors form an angle of 177.8°. The cyclopentadienyl rings are twisted 10.4 (3)° from the eclipsed conformation.

Introduction. Since the discovery of ferrocene (Kealy & Pauson, 1951; Miller, Tebboth & Tremaine, 1952), considerable interest has been directed toward preparation of bridged species, with the first being 1,3-(1,1'-ferrocenediyl)-1-propanone (Rinehart & Curby, 1957; Rosenblum, 1953) prepared from an acid-catalyzed cyclization of 3-ferrocenylpropionic acid; the X-ray structure was reported by Jones, Marsh & Richards (1965). The title compound (structure I) is the major product of an attempted synthesis of an ansa-bridged ferrocene derivative (structure II). The MS and elemental analyses were consistent with either structure (Fig. 1). The ¹H 400 MHz NMR spectra indicated structure (I) since the integration of 7:2 accounted for the splitting of the cyclopentadienyl H

atoms as well as an integration of 1 for the hydroxyl H atom. The ¹H NMR spectrum of the alkyl region was second order. The ¹³C and ¹³C DEPT (Derome, 1987) NMR spectra eliminated structure (II) as a possibility; however, the difficulties associated with the observation of quaternary C atoms made assignment to structure (I) inconclusive. The molecule was concluded to exist 100% as the lactol because no carbonyl stretch was observed by IR spectroscopy. Therefore, a single-crystal X-ray structure determination was undertaken to substantiate the ¹H NMR integration results.

Experimental. The *N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex of 1,1'-dilithioferrocene was prepared and found to react in high yield with CO₂ and benzophenone (Rausch & Ciappenelli, 1967). The reaction of this material with various diketones is being investigated as a new method to annulate the cyclopentadienyl rings of the ferrocene nucleus.

The cyclic 1,5-diketone, 1,5-cyclooctadione (Kulkarni, Rao & Patil, 1982) reacts with the 1,1'-dilithioferrocene–TMEDA complex in hexane to give the title compound. Crystals, m.p. 414.5–415.5 K

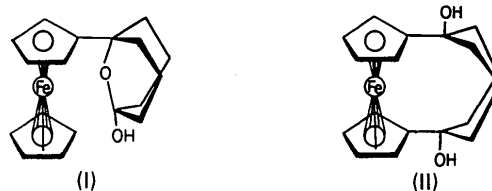


Fig. 1. Possible structures from the reaction of 1,1'-dilithioferrocene with 1,5-cyclooctadione.

* Reactions of 1,1'-Dilithioferrocene with Diketones.

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uncorrected, suitable for diffraction studies were obtained as plates by recrystallization from 2,2,4-trimethylpentane by slow cooling from 360–300 K.

Intensity data were obtained from an orange fragment of dimensions 0.08 × 0.32 × 0.44 mm mounted in random orientation on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined at 299 K by a least-squares fit to setting angles of 25 reflections having $12 < \theta < 13^\circ$. One octant of data having $2 \leq 2\theta \leq 54^\circ$, $0 \leq h \leq 36$, $0 \leq k \leq 15$, $0 \leq l \leq 10$ was measured using graphite-monochromatized Mo K α radiation. The ω – 2θ scans were made at speeds ranging from 0.45 to 4.0° min⁻¹ to measure all significant data with approximately equal relative precision. Three standard reflections (600, 060, 004) had 1.6% variation during data collection, thus no decay correction was applied. Of the 3528 unique data measured, 1591 had $F_o^2 > 3\sigma(F_o^2)$, and were used in the refinement. Data were corrected for background, Lorentz, polarization and absorption effects. Absorption corrections were applied using an empirical procedure based upon ψ scans for reflections near $\chi = 90^\circ$; the minimum relative transmission coefficient was 0.8495.

The structure was solved by heavy-atom methods and refined by full-matrix least squares based upon F , with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ using the Enraf–Nonius SDP (Frenz, 1985), scattering factors of Cromer & Waber (1974), and anomalous coefficients of Cromer (1974). Non-H atoms were refined anisotropically; the hydroxyl H atom was judged by difference maps to be disordered, and was fixed in two half-populated positions; all other H atoms were placed in calculated positions with C–H distance 0.95 Å. Final $R = 0.036$, $wR = 0.037$, $S = 1.570$ for 191 variables. Largest shift $< 0.01\sigma$ in the final cycle, maximum residual density 0.25 e Å⁻³, minimum -0.30 e Å⁻³, extinction coefficient $g = 4.6(9) \times 10^{-8}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c .

Discussion. The fractional coordinates of the title compound are given in Table 1. Fig. 2 is a perspective drawing showing the atom numbering. Selected distances, angles and torsion angles are presented in Table 2.*

The structure of the title compound exhibits typical ferrocene geometry; the two Cp rings are planar with maximum deviation 0.007(4) Å, and parallel, forming

* Lists of H-atom coordinates and thermal parameters, distances and angles, anisotropic thermal parameters, structure-factor amplitudes, torsion angles and least-squares-planes' data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44612 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Coordinates and equivalent isotropic thermal parameters

	x	y	z	$B_{eq}^*(\text{Å}^2)$
Fe	0.67998 (2)	0.25151 (5)	0.14874 (6)	2.281 (8)
O1	0.57497 (8)	0.2984 (2)	0.3478 (3)	2.22 (5)
O2	0.52528 (9)	0.4359 (2)	0.3933 (3)	3.21 (6)
C1	0.6296 (1)	0.1654 (3)	0.2638 (4)	2.16 (7)
C2	0.6191 (1)	0.1730 (3)	0.0998 (4)	2.70 (8)
C3	0.6567 (1)	0.1251 (3)	0.0150 (5)	3.13 (9)
C4	0.6898 (1)	0.0867 (3)	0.1243 (5)	3.08 (9)
C5	0.6733 (1)	0.1113 (3)	0.2774 (5)	2.76 (8)
C6	0.5982 (1)	0.1990 (3)	0.3984 (4)	2.43 (7)
C7	0.6268 (1)	0.2226 (3)	0.5462 (4)	3.5 (1)
C8	0.6006 (1)	0.2839 (4)	0.6761 (5)	4.3 (1)
C9	0.5710 (1)	0.3762 (3)	0.6081 (4)	3.31 (9)
C10	0.5437 (1)	0.3410 (3)	0.4637 (4)	2.42 (8)
C11	0.5612 (1)	0.1093 (3)	0.4182 (5)	3.60 (9)
C12	0.5214 (1)	0.1427 (3)	0.5290 (6)	4.4 (1)
C13	0.5049 (1)	0.2596 (3)	0.4918 (5)	3.20 (8)
C14	0.6760 (2)	0.4095 (3)	0.2256 (5)	4.2 (1)
C15	0.6725 (2)	0.4047 (3)	0.0586 (5)	4.2 (1)
C16	0.7137 (2)	0.3570 (3)	0.0033 (5)	4.5 (1)
C17	0.7420 (1)	0.3303 (4)	0.1311 (5)	4.6 (1)
C18	0.7187 (2)	0.3638 (3)	0.2691 (5)	4.4 (1)

* B_{eq} , for atoms refined anisotropically, is defined by the equation:

$$B_{eq} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}).$$

Table 2. Selected bond distances (Å), angles (°) and torsion angles (°)

C1–C6	1.516 (4)	C13–C10	1.515 (4)
C6–O1	1.451 (3)	C10–C9	1.520 (4)
C6–C11	1.537 (4)	C10–O2	1.407 (3)
C11–C12	1.541 (5)	C10–O1	1.433 (3)
C12–C13	1.537 (4)	C7–C8	1.532 (4)
C6–C7	1.530 (4)	C8–C9	1.528 (5)
C1–C6–O1	106.2 (2)	C7–C8–C9	111.3 (3)
C6–C7–C8	114.7 (3)	C8–C9–C10	112.7 (3)
C6–O1–C10	113.0 (2)	C9–C10–C13	116.1 (3)
C6–C11–C12	113.3 (3)	O1–C10–O2	104.1 (2)
C11–C12–C13	110.6 (3)	O2–C10–C9	107.8 (3)
C12–C13–C10	114.4 (3)	O2–C10–C13	109.2 (2)
C1–C6–O1–C10	-180.0 (7)	C6–O1–C10–O2	179.7 (2)
C1–C6–C11–C12	-168.8 (3)	O1–C10–C13–C12	51.9 (4)
C1–C6–C7–C8	165.6 (3)	O1–C10–C9–C8	-55.9 (3)

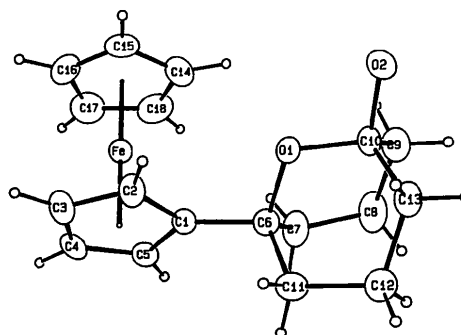


Fig. 2. ORTEP drawing (Johnson, 1965) of the molecule, representing heavy atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radius. The half-populated hydroxy H atoms are not shown.

a dihedral angle of $2.7(20)^\circ$. The Fe atom lies $1.641(1) \text{ \AA}$ from the plane of Cp1 (C1–C5) and $1.647(1) \text{ \AA}$ from the plane of Cp2 (C14–C18). Fe–C distances range from $2.030(3)$ – $2.042(3) \text{ \AA}$. The two Cp rings are nearly eclipsed, forming a twist angle of $10.4(3)^\circ$ (average of five C–Cp–Cp–C torsion-angle magnitudes, where Cp are ring centroids). The Cp1–Fe–Cp2 angle is 177.8° . Bulky substituents directly bound to the ferrocene moiety have been reported with larger distortions from ideal geometry. The crystal structure of 1-(1-hydroxy-1-phenylpropyl)-2,1'-trimethyleneferrocene (Lecomte, Dusaosoy, Protas, Moïse & Tirouflet, 1973) shows a Cp1–Fe–Cp2 angle of 170° . Similarly, 1,1',3,3'-tetra-*tert*-butylferrocene (Kaluski, Gusev, Kalinin & Struchkov, 1972) has a Cp1–Fe–Cp2 angle of 173° .

The two fused oxacyclohexane rings which comprise the lactol exhibit typical chair conformations. There is probably a favorable dipolar interaction which accounts for close interaction [$3.515(2) \text{ \AA}$] between O1 and the positively charged Fe atom. The Fe–C1–C6–O1 torsion angle of the title compound is $54.5(4)^\circ$, whereas 1-(1-hydroxy-1-phenylpropyl)-2,1'-trimethyleneferrocene contains an analogous torsion angle of $42.5(14)^\circ$ (Lecomte *et al.*, 1973).

The hydroxy group O2 forms two independent hydrogen-bonding contacts about point-symmetry elements with O2 of other molecules, $2.804(4) \text{ \AA}$ to that at $1-x, 1-y, 1-z$ and $2.838(4) \text{ \AA}$ to that at $1-x, y, \frac{1}{2}-z$, with the H atom half-populated in each. O–H...O angles are *ca* 153° for the hydrogen bond disordered

about the center, and *ca* 170° for that disordered about the twofold axis.

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Structure of Di[bis(1,4,7,10-tetraoxacyclododecane)sodium] Tetrachlorodioxouranate(VI)–Methanol (1/2), $[\text{Na}(\text{12-crown-4})_2]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{MeOH}^*$

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Abstract. $[\text{Na}(\text{C}_8\text{H}_{16}\text{O}_4)_2]_2[\text{UCl}_4\text{O}_2] \cdot 2\text{CH}_3\text{OH}$, $M_r = 1147$, orthorhombic, *Pbca*, $a = 14.393(3)$, $b = 23.223(5)$, $c = 14.909(3) \text{ \AA}$, $V = 4983.0 \text{ \AA}^3$, $Z = 4$, $D_x = 1.53 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 33.8 \text{ cm}^{-1}$, $F(000) = 2472$, $T = 293 \text{ K}$, final $R = 0.030$ for 2097 observed [$F_o \geq 5\sigma(F_o)$] reflections. The cations have no crystallographically imposed symmetry and consist of Na ions coordinated to all four O atoms of two unique crown ethers in a square antiprismatic

geometry. The Na–O separations average $2.49(2) \text{ \AA}$. The tetrachlorodioxouranate(VI) dianions are pseudo-octahedral and reside on crystallographic centers of inversion. The bonding parameters are normal. The solvent molecules are hydrogen bonded to the Cl atoms of the anions and are disordered.

Introduction. In the presence of benzo-15-crown-5, the slow aerial oxidation of a solution of UCl_3 in tetrahydrofuran (THF) and incorporation of Na^+ from the glass container resulted in the crystallization of $[\text{Na}(\text{benzo-15-crown-5})]_2[\text{UO}_2\text{Cl}_4]$, which has been

* *f*-Element/Crown Ether Complexes 18. Part 17: Rogers, Voss & Etzenhouser (1987).