Crystal structure of 1,6-di(ferrocenyl)-3,4-dihydroxy-hexa-2,4-diene-1,6-dion, $\text{Fe}_2(\text{C}_5\text{H}_5)_2(\text{C}_{16}\text{H}_{12}\text{O}_4)$

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Abstract

$\text{C}_{26}\text{H}_{22}\text{Fe}_2\text{O}_4$, monoclinic, $P12_1/n1$ (No. 14), $a = 5.9905(2)$ Å, $b = 15.0253(4)$ Å, $c = 12.0497(4)$ Å, $\beta = 90.945(1)^\circ$, $V = 1084.4$ Å³, $Z = 2$, $R_{\text{int}}(F) = 0.038$, $wR_{\text{ref}}(F^2) = 0.080$, $T = 200$ K.

Source of material

The title complex was synthesized from acetylferrocene, potassium hydride and diethyloxalate in thf, as described in [1]. Violet plates were obtained from a concentrated solution of the title compound in dichloromethane.

Discussion

The title molecule $\text{Fe}_2(\text{C}_5\text{H}_5)_2(\text{C}_{16}\text{H}_{12}\text{O}_4)$ **1** possesses an inversion centre (figure). The bond lengths and bond angles clearly show that the title complex has also in the solid state the keto enol structure and that the two hydroxy groups are in 3,4 positions of the hexadiene-dion rather than in 1,6. Important bond lengths and bond angles are: $d(\text{C1}—\text{C6}) = 1.458(3)$ Å, $d(\text{C6}—\text{O1}) = 1.258(3)$ Å, $d(\text{C6}—\text{C7}) = 1.447(3)$ Å, $d(\text{C7}—\text{C8}) = 1.346(3)$ Å, $d(\text{C8}—\text{O2}) = 1.335(3)$ Å, $d(\text{C8}—\text{C8}') = 1.474(3)$ Å, $\angle \text{O1}—\text{C6}—\text{C7} = 120.6(2)^\circ$, $\angle \text{C6}—\text{C7}—\text{C8} = 120.5(2)^\circ$, $\angle \text{C7}—\text{C8}—\text{O2} = 123.2(2)^\circ$, $\angle \text{C7}—\text{C8}—\text{C8}' = 123.7(2)^\circ$. The bond lengths in **1** are very similar to those in a bis(palladium) complex of the dianion of **1** — $(1-2\text{H}^+)[\text{Pd}(\text{Cl})\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3]_2$ [2] — with the exception that in that complex the four C—O distances are almost identical (1.282(4) Å, 1.279(4) Å), as expected. In the structure of **1**,

there is no symmetrical hydrogen bridge between the carbonyl groups. The bond length of $\text{O2}—\text{H82}$ is 0.88(3) Å while the distance between H82 and the acceptor O1 is 1.70(3) Å. The bond angle $\angle \text{O2}—\text{H82}—\text{O1}$ is $155(3)^\circ$. The angles between the least-square plane of O1, O2, C6, C7, and C8 and the C_5H_5 units are $9.58(13)^\circ$ and $10.22(17)^\circ$, respectively, indicating slight deviation from coplanarity. A stronger deviation is found in methyl ferrocenemonocarboxylate [3] for the ester and C_5H_5 units ($13.07(18)^\circ$, $11.52(17)^\circ$).

Table 1. Data collection and handling.

Crystal:	black-violet prism, size $0.02 \times 0.03 \times 0.25$ mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ :	13.69 cm^{-1}
Diffractionmeter, scan mode:	Kappa CCD, φ
$2\theta_{\text{max}}$:	54.94°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	18698, 2479
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1837
$N(\text{param})_{\text{refined}}$:	189
Programs:	SIR97 [4], SHELXL-97 [5], PLATON [6], ORTEP-III [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(82)	4e	−0.359(5)	0.056(2)	0.954(3)	0.06(1)
H(2)	4e	−0.375(5)	0.288(2)	0.719(2)	0.036(7)
H(3)	4e	−0.149(4)	0.371(2)	0.586(2)	0.034(7)
H(4)	4e	0.234(5)	0.305(2)	0.588(3)	0.047(8)
H(5)	4e	0.233(5)	0.181(2)	0.726(2)	0.044(8)
H(7)	4e	0.133(4)	0.093(2)	0.878(2)	0.024(6)
H(9)	4e	−0.211(6)	0.426(2)	0.919(3)	0.08(1)
H(10)	4e	0.028(5)	0.310(2)	1.004(3)	0.06(1)
H(11)	4e	0.389(5)	0.314(2)	0.921(3)	0.06(1)
H(12)	4e	0.393(6)	0.439(2)	0.782(3)	0.08(1)
H(13)	4e	0.007(6)	0.503(3)	0.780(3)	0.09(1)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Fe	4e	0.03557(6)	0.32821(2)	0.78506(3)	0.0275(2)	0.0309(2)	0.0346(2)	-0.0006(2)	-0.0016(1)	0.0077(2)
O(1)	4e	-0.3779(3)	0.1399(1)	0.8588(2)	0.0217(8)	0.0336(9)	0.040(1)	0.0014(7)	0.0011(7)	0.0050(8)
O(2)	4e	-0.2891(2)	0.0208(1)	1.0006(2)	0.0170(8)	0.0317(9)	0.039(1)	0.0012(7)	0.0032(7)	0.0084(8)
C(1)	4e	-0.0999(4)	0.2067(2)	0.7510(2)	0.027(1)	0.030(1)	0.028(1)	0.002(1)	-0.002(1)	0.003(1)
C(2)	4e	-0.2341(4)	0.2755(2)	0.7017(2)	0.030(1)	0.034(1)	0.032(2)	0.003(1)	-0.003(1)	0.005(1)
C(3)	4e	-0.1000(4)	0.3232(2)	0.6277(2)	0.039(1)	0.035(1)	0.033(2)	0.003(1)	-0.003(1)	0.011(1)
C(4)	4e	0.1164(5)	0.2849(2)	0.6292(2)	0.040(2)	0.043(2)	0.033(2)	0.005(1)	0.007(1)	0.010(1)
C(5)	4e	0.1201(4)	0.2138(2)	0.7052(2)	0.032(1)	0.037(1)	0.036(2)	0.007(1)	0.004(1)	0.008(1)
C(6)	4e	-0.1740(4)	0.1449(2)	0.8362(2)	0.028(1)	0.025(1)	0.027(1)	-0.001(1)	-0.001(1)	-0.003(1)
C(7)	4e	-0.0120(4)	0.0890(2)	0.8930(2)	0.018(1)	0.026(1)	0.033(1)	0.0005(9)	0.003(1)	0.002(1)
C(8)	4e	-0.0772(3)	0.0302(1)	0.9702(2)	0.017(1)	0.021(1)	0.031(1)	-0.0011(8)	0.0003(9)	-0.0044(9)
C(9)	4e	-0.0731(6)	0.4142(2)	0.9045(3)	0.042(2)	0.064(2)	0.067(2)	-0.004(2)	0.001(2)	-0.031(2)
C(10)	4e	0.0630(6)	0.3477(2)	0.9529(3)	0.064(2)	0.055(2)	0.036(2)	-0.019(2)	-0.004(2)	0.001(2)
C(11)	4e	0.2738(5)	0.3523(2)	0.9055(3)	0.043(2)	0.054(2)	0.056(2)	-0.006(2)	-0.017(2)	0.007(2)
C(12)	4e	0.2708(6)	0.4214(2)	0.8268(3)	0.046(2)	0.050(2)	0.061(2)	-0.014(2)	-0.007(2)	0.009(2)
C(13)	4e	0.0569(6)	0.4600(2)	0.8257(3)	0.069(2)	0.034(2)	0.065(2)	-0.003(2)	-0.020(2)	-0.001(2)

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