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(*E*)-1,3-Diferrocenyl-2-buten-1-one–Water (4/1)

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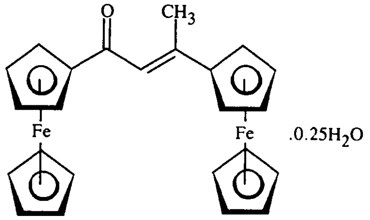
Abstract

The title compound, μ-[(*E*)-1,3-di-η^5-cyclopentadienyl-2-buten-1-one]bis(η^5-cyclopentadienyliron)–water (4/1), [$Fe_2(C_5H_5)_2(C_{14}H_{12}O)$].0.25$H_2O$, has two independent [$Fe_2(C_5H_5)_2(C_{14}H_{12}O)$] molecules in the asymmetric unit. Pairs of one of these molecules form dimers linked by hydrogen bonds *via* a water molecule occupying either of two sites related by a centre of symmetry.

Comment

The formation of the title compound, (I), is assumed to result from the self-condensation of acetylferrocene due to incomplete enolate formation, a consequence of the high reactivity of the enolate moiety of acetylferrocene towards electrophilic centres. The final product is obtained *via* elimination of a proton, catalyzed by the addition of dilute HCl during the work-up procedure.



(I)

The structure of (I) contains two crystallographically independent [$Fe_2(C_5H_5)_2(C_{14}H_{12}O)$] molecules (*A* and *B*, shown in Figs. 1 and 2, respectively) in the asymmetric unit. The two *A*-type molecules in the unit cell are linked by hydrogen bonds *via* a single water molecule in a twofold disordered position (see Fig. 1).

The average Fe—C bond distances of both ferrocenyl fragments of the independent molecules *A* and *B* are identical within experimental error [2.037 (5) Å], while the average C—C bond distance for the four unsubstituted cyclopentadienyl rings of *A* and *B* [1.398 (7) Å] differs considerably from the corresponding average for the four substituted cyclopentadienyl rings [1.419 (6) Å].

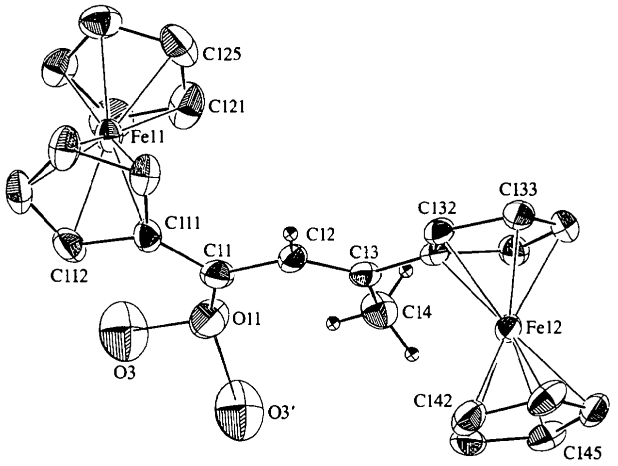


Fig. 1. The structure of molecule *A* of (I) showing the numbering scheme and displacement ellipsoids of 30% probability. Ferrocenyl H atoms have been omitted for clarity. The primed atom is generated through the centre of symmetry.

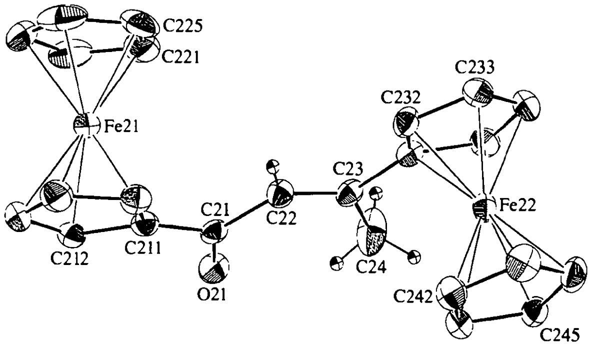


Fig. 2. The structure of molecule *B* of (I) showing the numbering scheme and displacement ellipsoids of 30% probability. Ferrocenyl H atoms have been omitted for clarity.

Similar differences were observed in acyl-substituted ferrocenes (Cameron & Cordes, 1979; Barnes, Bell, Glidewell & Howie, 1990), as well as in the structure of 1-ferrocenyl-3-hydroxy-2-buten-1-one, where a difference of 0.027 (8) Å between the average C—C bond distances under discussion was observed (Bell, Crayston, Glidewell, Mazid & Hursthouse, 1992). The average C═C double-bond distance in *A* and *B* [1.354 (6) Å] is in good agreement with the range of 1.343 (4)–1.392 (3) Å (Jones, 1976; Tønnesen, Karlsen & Mostad, 1982) observed for C═C double bonds in compounds of similar structure such as enolized asymmetric 1,3-diketones. The accepted range for the C—O bond distance in enolized asymmetric 1,3-diketones is 1.269 (4)–1.283 (3) Å (Jones, 1976; Tønnesen *et al.*, 1983), while it varies between 1.212 (4) and 1.221 (4) Å in the non-enolized counterparts (Gyepes, Glowiak, Toma & Soldanova, 1984; Gyepes, Glowiak & Toma, 1986; Mullica, Karban & Grossie, 1987). The average value of 1.233 (5) Å for the C—O bond distance in molecules *A* and *B* of the title compound is more comparable with the latter case, which suggests that the carbonyl group has basically the same structural nature as in a compound like ferrocenophanedione.

Both *A* and *B* take on the *E* isomeric form in the solid state, with the angles C131—C13—C14 (in *A*) and C231—C23—C24 (in *B*) both equal to 116.1 (4)°, which compares well with the corresponding angle of 116.3 (5)° between the methyl and hydroxy groups in 1-ferrocenyl-3-hydroxy-2-buten-1-one (Bell *et al.*, 1992). The cyclopentadienyl rings of both ferrocenyl fragments in molecules *A* and *B* are in the usual eclipsed conformation, as was previously observed in a ferrocene-containing β-diketonato complex of rhodium(I) (Lamprecht, Swarts, Conradie & Leipoldt, 1993).

Experimental

The title compound was isolated as a by-product during the preparation of the β-diketone diferrocenoylmethane (DFcM) [FcC(O)CH$_2$C(O)Fc] (Fc is ferrocene). The latter compound was prepared utilizing lithiumdiisopropylamide (LDA) as a strong sterically-hindered base under rigorous Schlenck conditions. A light-yellow solution of LDA was prepared by adding a 1.710 *M* solution of *n*-butyllithium in dry hexane (4.24 ml, 7.25 mmol) to an ice-cooled solution of dry freshly distilled diisopropylamine (1.01 ml, 7.20 mmol) in dry tetrahydrofuran (THF) (15 ml). A solution of acetylferrocene, [FcC(O)CH$_3$] (1.46 g, 6.40 mmol), in dry THF (10 ml) was slowly added to the LDA solution and the mixture stirred at room temperature for *ca* 20 min before a solution of methylferrocenoate, [FcC(O)OCH$_3$] (1.48 g, 6.00 mmol), in dry THF (10 ml) was added. The reaction mixture was stirred for 4 h at room temperature, quenched with *ca* 1 *M* HCl (50 ml) and extracted with diethyl ether (5 × 100 ml). The combined ether fractions were washed (distilled water), dried (MgSO$_4$) and the solvent removed. Preparative HPLC [silica gel 60, ether:hexane (2:3 *v*/*v*)] yielded the β-diketone DFcM (0.80 g, R_f 0.71, *ca* 30% yield), as well as the title compound (0.53 g, R_f 0.55, *ca* 20% yield). Diamond-shaped crystals were obtained from a concentrated ether solution at 255 K. ^{1}H NMR (acetone-d_6): δ 2.55 (*d*, 3H, $^4J_{\rm H-H}$ = 1 Hz, CH$_3$), 6.89 (*q*, 1H, $^4J_{\rm H-H}$ = 1 Hz, CH). The density D_m was measured in NaI/H$_2$O solution.

Crystal data

[Fe$_2$(C$_5$H$_5$)$_2$(C$_{14}$H$_{12}$O)].-0.25H$_2$O
M_r = 442.62
Triclinic
$P\overline{1}$
a = 12.202 (1) Å
b = 12.364 (2) Å
c = 13.290 (2) Å
α = 79.80 (1)°
β = 88.90 (1)°
γ = 82.60 (1)°
V = 1956.9 (5) Å^3
Z = 4
D_x = 1.502 Mg m^{-3}
D_m = 1.488 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–20°
μ = 1.494 mm^{-1}
T = 293 (2) K
Diamond-shaped
0.32 × 0.28 × 0.25 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7193 measured reflections
6844 independent reflections
4526 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.0204
$\theta_{\rm max}$ = 25°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R(F)$ = 0.0398
$wR(F^2)$ = 0.1203
S = 1.110
6842 reflections
507 parameters
H atoms riding, except for those of the water molecule (see text)
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.66P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = 0.059
$\Delta\rho_{\rm max}$ = 0.410 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.562 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Fe11	0.37606 (5)	0.31144 (5)	0.37017 (5)	0.0455 (2)
Fe12	−0.12505 (4)	0.21043 (5)	0.05087 (4)	0.0414 (2)
Fe21	0.15345 (5)	−0.15817 (5)	0.42008 (4)	0.0441 (2)
Fe22	0.65578 (4)	−0.30881 (5)	0.13861 (4)	0.0385 (2)
O11	0.0759 (3)	0.3411 (4)	0.4012 (3)	0.0959 (14)
C11	0.1351 (4)	0.2838 (4)	0.3486 (3)	0.0582 (12)
C12	0.1030 (3)	0.2665 (4)	0.2487 (3)	0.0491 (11)
C13	0.0190 (3)	0.3237 (3)	0.1875 (3)	0.0430 (10)
C14	−0.0548 (4)	0.4206 (4)	0.2129 (4)	0.0670 (14)
O21	0.2715 (2)	0.0153 (2)	0.1787 (2)	0.0498 (7)
C21	0.2837 (3)	−0.0800 (3)	0.2263 (3)	0.0381 (9)
C22	0.3906 (3)	−0.1501 (3)	0.2449 (3)	0.0419 (9)
C23	0.4916 (3)	−0.1259 (3)	0.2134 (3)	0.0396 (9)
C24	0.5129 (4)	−0.0170 (4)	0.1522 (4)	0.078 (2)
C111	0.2434 (4)	0.2279 (4)	0.3890 (3)	0.0508 (11)
C112	0.2876 (5)	0.2353 (5)	0.4853 (3)	0.0675 (14)
C113	0.3973 (5)	0.1844 (4)	0.4926 (4)	0.0709 (15)
C114	0.4235 (4)	0.1435 (4)	0.4018 (4)	0.0661 (14)
C115	0.3285 (4)	0.1712 (3)	0.3367 (4)	0.0563 (12)
C121	0.3278 (6)	0.4607 (5)	0.2834 (5)	0.088 (2)
C122	0.3640 (5)	0.4738 (4)	0.3818 (5)	0.078 (2)
C123	0.4742 (4)	0.4265 (4)	0.3930 (4)	0.0670 (14)
C124	0.5065 (5)	0.3845 (5)	0.3049 (5)	0.078 (2)
C125	0.4159 (6)	0.4055 (5)	0.2373 (4)	0.085 (2)
C131	−0.0005 (3)	0.2929 (3)	0.0890 (3)	0.0381 (9)
C132	0.0435 (3)	0.1934 (4)	0.0529 (3)	0.0444 (10)
C133	0.0052 (3)	0.1990 (4)	−0.0466 (3)	0.0550 (12)
C134	−0.0632 (4)	0.3019 (4)	−0.0756 (3)	0.0578 (12)
C135	−0.0675 (4)	0.3588 (4)	0.0071 (3)	0.0506 (11)
C141	−0.2237 (4)	0.1709 (5)	0.1748 (4)	0.072 (2)
C142	−0.1739 (4)	0.0754 (5)	0.1418 (4)	0.0680 (14)
C143	−0.2063 (4)	0.0787 (4)	0.0409 (4)	0.0637 (14)
C144	−0.2761 (3)	0.1766 (4)	0.0113 (4)	0.0572 (12)
C145	−0.2871 (4)	0.2348 (4)	0.0923 (4)	0.0591 (12)
C211	0.1865 (3)	−0.1316 (3)	0.2686 (3)	0.0398 (9)
C212	0.0819 (3)	−0.0705 (4)	0.2873 (3)	0.0472 (10)
C213	0.0119 (4)	−0.1470 (4)	0.3353 (3)	0.0567 (12)
C214	0.0701 (4)	−0.2542 (4)	0.3447 (3)	0.0584 (12)
C215	0.1781 (4)	−0.2459 (4)	0.3046 (3)	0.0487 (10)
C221	0.2739 (5)	−0.1039 (6)	0.4943 (4)	0.078 (2)

C222	0.1738 (6)	−0.0524 (5)	0.5186 (4)	0.077 (2)
C223	0.1096 (5)	−0.1305 (6)	0.5632 (4)	0.077 (2)
C224	0.1693 (6)	−0.2347 (6)	0.5667 (4)	0.088 (2)
C225	0.2749 (5)	−0.2164 (6)	0.5243 (4)	0.084 (2)
C231	0.5891 (3)	−0.2100 (3)	0.2371 (3)	0.0410 (9)
C232	0.5886 (4)	−0.3248 (3)	0.2805 (3)	0.0482 (10)
C233	0.6984 (4)	−0.3770 (4)	0.2863 (3)	0.0567 (12)
C234	0.7684 (4)	−0.2964 (4)	0.2470 (3)	0.0565 (12)
C235	0.7021 (3)	−0.1947 (4)	0.2170 (3)	0.0498 (11)
C241	0.5663 (3)	−0.2652 (4)	0.0055 (3)	0.0499 (11)
C242	0.5598 (4)	−0.3772 (4)	0.0498 (3)	0.0548 (12)
C243	0.6677 (4)	−0.4343 (4)	0.0569 (4)	0.0594 (12)
C244	0.7408 (4)	−0.3585 (4)	0.0174 (3)	0.0550 (12)
C245	0.6788 (3)	−0.2547 (4)	−0.0143 (3)	0.0469 (10)
O3†	0.9070 (10)	0.5100 (8)	0.4659 (8)	0.137 (4)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

O11—C11	1.239 (6)	O21—C21	1.226 (4)
C11—C12	1.452 (6)	C21—C22	1.470 (5)
C11—C111	1.473 (6)	C21—C211	1.475 (5)
C12—C13	1.362 (6)	C22—C23	1.347 (5)
C13—C131	1.458 (5)	C23—C231	1.475 (5)
C13—C14	1.488 (6)	C23—C24	1.495 (6)
O11—C11—C12	123.5 (5)	C22—C23—C231	120.0 (4)
O11—C11—C111	119.3 (4)	C22—C23—C24	123.9 (4)
C12—C11—C111	117.2 (4)	C231—C23—C24	116.1 (4)
C13—C12—C11	128.1 (4)	C115—C111—C112	106.8 (4)
C12—C13—C131	119.8 (4)	C115—C111—C11	127.9 (4)
C12—C13—C14	124.0 (4)	C132—C131—C135	106.0 (4)
C131—C13—C14	116.1 (4)	C135—C131—C13	126.1 (4)
O21—C21—C22	124.7 (4)	C215—C211—C212	107.3 (4)
O21—C21—C211	119.7 (4)	C215—C211—C21	128.6 (4)
C22—C21—C211	115.6 (3)	C235—C231—C232	106.4 (4)
C23—C22—C21	128.4 (4)	C235—C231—C23	126.9 (4)

H-atom positions were calculated riding on the parent C atom, with C—H distances of 0.96 (cyclopentadienyl), 0.93 (methyl) and 0.90 Å (methylene), and refined with an overall $U_{\rm iso}$ of 0.07 Å^2.

Data collection: *CAD*-4 *Software* (Enraf--Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1313). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*trans*-1*R*,2*R*-Cyclohexanediamine-*N*,*N'*)(L-ascorbato-C^2,O^5)platinum(II)–Water (1/3)

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Abstract

In the title compound, $[Pt(C_6H_6O_6)(C_6H_{14}N_2)].3H_2O$, the dianionic ascorbate ligand forms a six-membered chelate ring coordinating to the Pt atom through O and C atoms. The Pt—N distance at the *trans* position of the C atom is slightly longer than that at the *trans* position of the O atom [2.093 (5) and 2.033 (5) Å, respectively]. Three water molecules link the carbonyl or hydroxyl groups of one ascorbate ligand with the amino group of another through hydrogen bonds surrounding the cyclohexane ring.

Comment

L-Ascorbic acid (H_2asc), which is one of the most important biomolecules and participates in electron-transfer systems *in vivo*, acts as a monobasic acid in general. Its crystal structure and those of the Na^+, Ca^{2+} and Tl^+ salts have already been reported (Hvoslef, 1968*a*,*b*, 1969; Hearn & Bugg, 1974; Hvoslef & Kjellevold, 1974; Hughes, 1973). The molecule may often behave as a dibasic acid (pK_1 = 4.26 and pK_2 = 11.64), however, and is oxidized by the removal of two electrons to crystallize as a dimeric form of dehydro-L-ascorbic acid (Hvoslef, 1972), with an intramolecular O6···C3