Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(\mathring{A}^2)$

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

	x	y	z	B_{eq}
Cu	−0.14962 (5)	0.10383 (3)	−0.17221 (2)	1.989 (6)
O1	0.1176 (4)	0.3298 (3)	−0.1253 (2)	4.76 (6)
N11	−0.2035 (3)	0.0290 (2)	−0.3485 (2)	2.09 (4)
N1	−0.3559 (3)	0.2187 (2)	−0.1643 (2)	2.48 (4)
C2	−0.4344 (4)	0.2054 (3)	−0.0605 (2)	3.07 (6)
C3	−0.2584 (4)	0.2092 (3)	0.0410 (2)	2.27 (5)
N4	−0.1453 (3)	0.1186 (2)	−0.0107 (2)	2.21 (4)
C5	−0.0501 (3)	0.0405 (3)	0.0402 (2)	1.94 (5)
O51	−0.0317 (3)	0.0236 (2)	0.1436 (1)	2.30 (3)
O103	0.2834 (6)	0.4552 (3)	0.1229 (3)	10.7 (1)
Cl	0.4084 (1)	0.41754 (7)	0.21281 (6)	3.40 (2)
O101	0.3973 (3)	0.2678 (2)	0.1740 (2)	4.34 (5)
O102	0.3451 (6)	0.4395 (4)	0.3150 (3)	10.3 (1)
O104	0.6141 (5)	0.5105 (4)	0.2425 (3)	8.9 (1)
N14	−0.2970 (3)	−0.1115 (2)	−0.5905 (2)	2.72 (5)
C12	−0.2476 (4)	−0.1144 (3)	−0.3890 (2)	2.39 (5)
C13	−0.2972 (4)	−0.1843 (3)	−0.5107 (2)	2.67 (6)
C15	−0.2475 (4)	0.0379 (3)	−0.5505 (2)	2.24 (5)
C16	−0.2038 (3)	0.1106 (3)	−0.4293 (2)	2.01 (5)
C17	−0.1623 (4)	0.2643 (3)	−0.3937 (2)	2.64 (6)
C18	−0.1655 (4)	0.3410 (3)	−0.4769 (2)	3.21 (6)
C19	−0.2023 (5)	0.2702 (3)	−0.5961 (2)	3.40 (6)
C20	−0.2423 (4)	0.1220 (3)	−0.6331 (2)	3.07 (6)

Table 2. *Selected geometric parameters* $(\mathring{A}, \,^{\circ})$

Cu—O1	2.139 (2)	Cu—O51^i	2.098 (2)
Cu—N4	1.916 (2)	Cu—N1	2.128 (2)
Cu—N11	2.001 (2)		
O1—Cu—N11	99.88 (8)	O1—Cu—N1	87.01 (1)
O1—Cu—N4	94.75 (9)	O1—Cu—O51^i	98.88 (10)
N11—Cu—N1	101.88 (9)	N11—Cu—N4	164.89 (9)
N11—Cu—O51^i	90.03 (8)	N1—Cu—N4	82.54 (9)
N1—Cu—O51^i	165.68 (8)	N4—Cu—O51^i	83.96 (8)

Symmetry code: (i) $-x, -y, -z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Program(s) used to solve structure: *MULTAN*11/84 (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SDP-Plus* (Frenz, 1985). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triple-Decker [Cp*Fe(C8H6)Fe(C8H7)]

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Abstract

The title compound, $[2(1,2,3,3a,6a-\eta)-1,4-\text{dihydro-pentalenyl}][\mu-(1,2,3,3a,6a-\eta:3a,4,5,6,6a-\eta)\text{pentalene}]-[1(\eta^5)-\text{pentamethylcyclopentadienyl}]\text{diiron}$, $[Fe_2(C_8H_7)-(C_{10}H_{15})(C_8H_6)]$, has a metallocenic structure with the two pentalene ligands adopting an eclipsed conformation. In the central pentalene ligand, all the peripheral bonds are of similar length whereas the bridge bond is longer; there are two significantly different Fe—C distances, *i.e.* a mean value of 2.121 (3) Å for the Fe—C_{bridge} distances and a mean value of 2.028 (3) Å for the distances from the Fe atoms to all other C atoms. In the terminal pentalene ligand, the C—C and C—Fe distances in the ring bonded to the Fe atom are all similar.

Comment

The detailed physical and structural characterization of binuclear complexes of the type $[\text{Cp}^*-M-\text{pentalene}-M-\text{Cp}^*]^{n+}$ (M = Fe, Co, Ni; n = 0, 1, 2; Cp* = η^5-pentamethylcyclopentadienyl) has been reported recently (Manríquez *et al.*, 1995). In these complexes, the mixed-valence iron derivative was found to be fully delocalized as demonstrated by ^{57}Fe Mössbauer spectroscopy. The salt exhibited a single intermediate-

value quadrupole doublet (between Fe^{2+} and Fe^{3+}) on a Mössbauer time scale to as low as 1.5 K. The possibility that polymers derived from pentalene might exhibit interesting electrical and/or magnetic properties associated with electron delocalization and electronic cooperative interactions in odd-electron systems prompted us to prepare, characterize and model the monomers. As part of this general structural study, we present here the title compound, (I), which can be envisioned as the smallest subunit of the polymers.

Me
Me—⟨⟩—Me
Me Fe Me

(I)
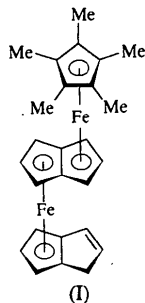
Few crystal structures of pentalene complexes have been described. In addition to those mentioned above, one nickel complex (Kitano, Kashiwagi & Kinoshita, 1973), one lithium complex (Stezowski, Hoier, Wilhelm, Clark & Schleyer, 1985), two iron complexes (Churchill & Lin, 1973; Bunel *et al.*, 1988) and five ruthenium complexes (Howard, Knox, Riera, Stone & Woodward, 1974; Howard, Knox, Stone, Szary & Woodward, 1974; Howard & Woodward, 1978; Howard, Stansfield & Woodward, 1979) have been reported. The five ruthenium complexes are polynuclear with the Ru atoms on the same side of the pentalene plane. The other metal complexes are dinuclear, similar to the title compound, with the two metal atoms on opposite sides of the pentalene plane.

The title compound, (I), has a metallocenic structure (Fig. 1). The two pentalene ligands adopt an eclipsed conformation. The dihedral angle between the two pentalene mean planes is 2.0 (1)°. The Cp* ligand is not totally eclipsed with respect to the central pentalene ligand. The dihedral angle between the Cp* mean plane and the central pentalene mean plane is 5.5 (1)° (Fig. 2). The Cp* and terminal pentalene ligands are planar but the central pentalene is slightly distorted showing a chair-like conformation; there is a local pseudo-twofold axis along the C21—C25 bond and a local pseudo-mirror plane along C23···C27. The Cremer & Pople (1975) total puckering amplitude, Q_T, is 0.076 (3). The dihedral angle between the tips (C26–C28 and C22–C24) and the middle (C22, C24, C21, C25, C26 and C28) of the chair are 4.7 (2) and 5.1 (2)°, respectively. In the peripheral bonds of the central pentalene ligand, the bond alternation is small, with the C—C bridge bond displaying a longer length. In the related binuclear iron pentalene complex (Bunel *et al.*,

1988), the same situation has also been observed, while in the homologous cobalt complex, the bond alternation is small in the whole pentalene moiety (Manríquez *et al.*, 1995). In the terminal pentalene, the ring bonded to the Fe atom shows all the bonds to be of similar length and consistent with the values described for the cyclopentadienide rings (like Cp*).
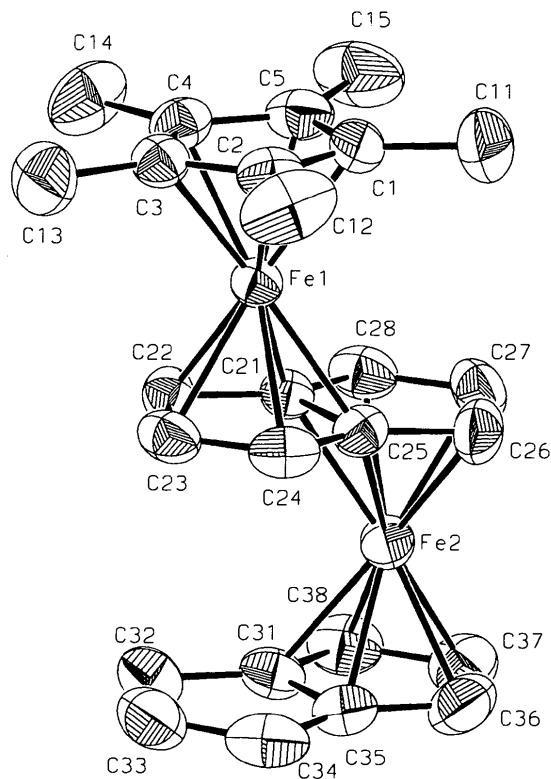

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The Fe-atom positions are nearly centered with respect to the ligand rings (Fig. 2). The slippage between the ring centroid and the projection of iron on the ring plane are 0.093 (6) for Fe1 and the central pentalene, 0.089 (6) for Fe2 and the central pentalene, 0.027 (13) for Fe2 and the terminal pentalene, and 0.018 (14) Å for Fe1 and the Cp* ligand. The Fe1—Cp* mean-plane distance is 1.643 (1), the Fe1–pentalene mean plane distance is 1.665 (1) and the Fe2–pentalene mean-plane distances are 1.667 (1) for the central and 1.656 (1) Å for the terminal pentalene moiety. The Fe—C distances from Fe1 to Cp* are all similar [mean value 2.037 (3) Å], as are the distances from Fe2 to the five Fe-bonded C atoms of the terminal pentalene ligand [mean value 2.049 (3) Å]. On the contrary, there are two distance values from the Fe atoms to the central pentalene C atoms, one corresponding to the iron and the bridge C atoms [mean value 2.121 (3) Å], and the other to the Fe atoms and the rest of the C atoms [mean value

2.028 (3) Å]. This situation has also been described for the previously mentioned binuclear iron complex (Bunel *et al.*, 1988).

The molecules are packed in the crystal in such a way that the ligands adopt two almost perpendicular orientations (Fig. 3). This means that there are no π interactions between the two molecules. This packing is different to that found in the other pentalene complexes showing molecular stacks.
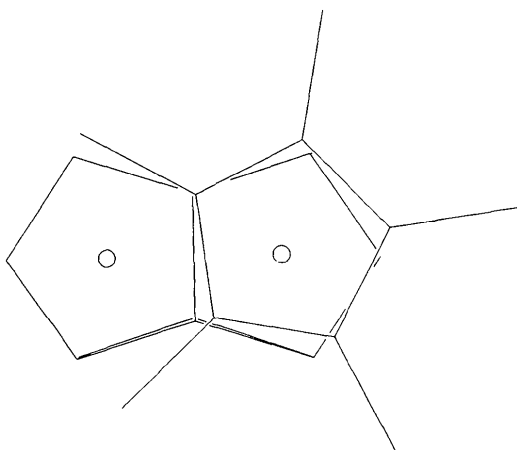

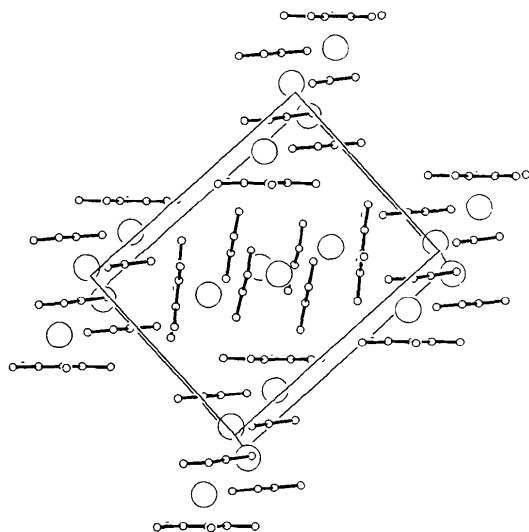Fig. 2. View perpendicular to the pentalene plane.

Fig. 3. View of the unit-cell packing.

Experimental

The title compound was prepared according to the method of Oelckers, Chávez, Manríquez & Román (1993). Suitable crystals were grown by slow evaporation from a hexane solution in an inert atmosphere. For the diffraction measurement, a crystal was mounted in a nitrogen-filled capillary.

Crystal data

[Fe$_2$(C$_8$H$_7$)(C$_{10}$H$_{15}$)(C$_8$H$_6$)]
M_r = 452.18
Monoclinic
$P2_1/n$
a = 11.216 (1) Å
b = 14.366 (2) Å
c = 12.837 (3) Å
β = 92.03 (1)°
V = 2067.1 (6) Å^3
Z = 4
D_x = 1.453 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11.44–13.92°
μ = 1.412 mm^{-1}
T = 293 (2) K
Prism
0.47 × 0.43 × 0.18 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.62, T_{max} = 0.78
3630 measured reflections
3630 independent reflections

2626 observed reflections
[$I > 2\sigma(I)$]
θ_{max} = 24.97°
h = -13 → 13
k = 0 → 17
l = 0 → 15
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0350
$wR(F^2)$ = 0.0916
S = 0.971
3630 reflections
255 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = -0.003
$\Delta\rho_{max}$ = 0.298 e Å^{-3}
$\Delta\rho_{min}$ = -0.302 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)

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

	x	y	z	U_{eq}
Fe1	0.09248 (4)	0.22506 (3)	0.80434 (3)	0.03423 (13)
Fe2	-0.06298 (4)	-0.01341 (3)	0.72019 (3)	0.04066 (15)
C1	0.2738 (3)	0.2397 (2)	0.8123 (3)	0.0527 (9)
C2	0.2211 (3)	0.2938 (2)	0.8901 (2)	0.0459 (8)
C3	0.1404 (3)	0.3576 (2)	0.8402 (2)	0.0426 (7)
C4	0.1451 (3)	0.3430 (2)	0.7315 (3)	0.0469 (8)
C5	0.2261 (3)	0.2716 (2)	0.7139 (3)	0.0507 (8)
C11	0.3663 (4)	0.1648 (3)	0.8294 (4)	0.092 (2)
C12	0.2471 (4)	0.2882 (3)	1.0055 (3)	0.0817 (14)
C13	0.0676 (4)	0.4299 (3)	0.8937 (3)	0.0718 (11)
C14	0.0743 (4)	0.3969 (3)	0.6483 (3)	0.0745 (12)
C15	0.2611 (4)	0.2357 (3)	0.6088 (3)	0.0865 (15)
C21	-0.0100 (2)	0.1278 (2)	0.7160 (2)	0.0352 (6)
C22	-0.0776 (3)	0.2065 (2)	0.7500 (3)	0.0416 (7)
C23	-0.0716 (3)	0.2060 (2)	0.8604 (3)	0.0485 (8)
C24	0.0060 (3)	0.1354 (2)	0.8988 (2)	0.0479 (8)
C25	0.0423 (3)	0.0824 (2)	0.8101 (2)	0.0389 (7)
C26	0.1077 (3)	0.0029 (2)	0.7753 (3)	0.0544 (9)
C27	0.1029 (3)	0.0031 (2)	0.6658 (3)	0.0578 (10)
C28	0.0264 (3)	0.0748 (2)	0.6272 (3)	0.0493 (8)
C31	-0.2462 (3)	-0.0146 (2)	0.7236 (3)	0.0480 (8)
C32	-0.3192 (3)	0.0640 (3)	0.7564 (3)	0.0576 (9)
C33	-0.3131 (3)	0.0628 (3)	0.8639 (3)	0.0697 (11)
C34	-0.2397 (4)	-0.0109 (3)	0.9061 (3)	0.0663 (11)

C35	−0.1967 (3)	−0.0605 (2)	0.8125 (3)	0.0503 (8)
C36	−0.1259 (4)	−0.1355 (2)	0.7797 (3)	0.0638 (10)
C37	−0.1318 (3)	−0.1370 (3)	0.6701 (3)	0.0643 (10)
C38	−0.2068 (3)	−0.0618 (3)	0.6334 (3)	0.0584 (9)

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

Fe1—C1	2.044 (3)	C1—C5	1.429 (5)
Fe1—C2	2.039 (3)	C1—C11	1.506 (5)
Fe1—C3	2.027 (3)	C2—C12	1.502 (5)
Fe1—C4	2.033 (3)	C3—C13	1.502 (5)
Fe1—C5	2.041 (3)	C4—C14	1.520 (5)
Fe1—C22	2.025 (3)	C5—C15	1.510 (5)
Fe1—C23	2.018 (3)	C21—C22	1.438 (4)
Fe1—C24	2.038 (3)	C21—C28	1.441 (4)
Fe1—C25	2.128 (3)	C21—C25	1.476 (4)
Fe1—C21	2.114 (3)	C22—C23	1.417 (5)
Fe2—C21	2.115 (3)	C23—C24	1.414 (5)
Fe2—C25	2.127 (3)	C24—C25	1.440 (4)
Fe2—C26	2.031 (3)	C25—C26	1.437 (4)
Fe2—C27	2.024 (3)	C26—C27	1.405 (5)
Fe2—C28	2.030 (3)	C27—C28	1.418 (5)
Fe2—C31	2.057 (3)	C31—C35	1.414 (5)
Fe2—C35	2.059 (3)	C31—C38	1.425 (5)
Fe2—C36	2.049 (4)	C31—C32	1.466 (5)
Fe2—C37	2.031 (3)	C32—C33	1.379 (5)
Fe2—C38	2.049 (3)	C33—C34	1.436 (6)
C1—C2	1.412 (5)	C34—C35	1.492 (5)
C2—C3	1.424 (4)	C35—C36	1.411 (5)
C3—C4	1.414 (4)	C36—C37	1.406 (5)
C4—C5	1.394 (5)	C37—C38	1.439 (5)
C2—C1—C5	107.2 (3)	C23—C24—C25	106.9 (3)
C2—C1—C11	126.4 (4)	C26—C25—C24	145.8 (3)
C5—C1—C11	126.3 (4)	C26—C25—C21	106.8 (3)
C1—C2—C3	108.1 (3)	C24—C25—C21	107.4 (3)
C1—C2—C12	126.7 (3)	C27—C26—C25	107.9 (3)
C3—C2—C12	125.2 (3)	C26—C27—C28	110.6 (3)
C4—C3—C2	107.6 (3)	C27—C28—C21	107.0 (3)
C4—C3—C13	126.4 (3)	C35—C31—C38	108.1 (3)
C2—C3—C13	125.9 (3)	C35—C31—C32	109.6 (3)
C5—C4—C3	108.4 (3)	C38—C31—C32	142.4 (3)
C5—C4—C14	126.1 (3)	C33—C32—C31	105.6 (3)
C3—C4—C14	125.5 (3)	C32—C33—C34	113.2 (4)
C4—C5—C1	108.6 (3)	C33—C34—C35	104.2 (3)
C4—C5—C15	126.0 (4)	C36—C35—C31	108.9 (3)
C1—C5—C15	125.4 (4)	C36—C35—C34	143.7 (4)
C22—C21—C28	145.3 (3)	C31—C35—C34	107.4 (3)
C22—C21—C25	107.3 (3)	C37—C36—C35	107.6 (3)
C28—C21—C25	107.4 (3)	C36—C37—C38	108.8 (3)
C23—C22—C21	107.0 (3)	C31—C38—C37	106.6 (3)
C24—C23—C22	111.0 (3)		

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1233). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(SS*,1S*,2R*)-1-(Hydroxymethyl)-2-(p-tolylsulfinyl)ferrocene

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Abstract

The title compound, (SS*,1S*,2R*)-[2-(p-tolylsulfinyl)-1-ferrocenyl]methanol, [Fe($C_{13}H_{13}O_2S$)(C_5H_5)], isolated as a racemic mixture, was synthesized *via* the rapid