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1,5-Diferrocenylnaphthalene

C. JOHN McADAM, BRIAN H. ROBINSON AND JIM SIMPSON

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. E-mail: jsimpson@alkali.otago.ac.nz

Abstract

The title compound, $[Fe_2(C_5H_5)_2(C_{20}H_{14})]$, was prepared by a palladium-catalyzed coupling reaction. The molecule lies about an inversion centre with the two ferrocenyl moieties bound to the 1 and 5 positions of the naphthalene unit and inclined at an angle of 47.0 (2)° with respect to the naphthalene mean plane.

Comment

As part of our continuing investigations on the formation of compounds in which redox centres are linked by conductive bridges (Elder, Robinson & Simpson, 1990; Robinson, Simpson & Worth, 1992; Duffy, McAdam, Robinson & Simpson, 1996), we have prepared 1,5-diferrocenylnaphthalene, (I), in yields of 10–20% by the palladium-catalyzed coupling of ferrocenyl zinc chloride with 1,5-diiodonaphthalene. The structure of the resulting product is the subject of this report.

(I)
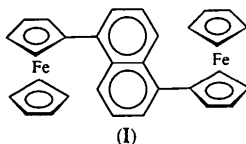
The structure of (I) consists of well separated molecules lying about inversion centres with all intermolecular contacts < 3.5 Å involving H atoms (Nardelli, 1983). The naphthalene-bound cyclopentadiene rings of the ferrocenyl groups are inclined at angles of 47.0 (2)° with respect to the naphthalene mean plane. In contrast, the outer naphthyl substituents in 2′,6′-diethyl-1,1′:5′,1″-trinaphthyl are inclined at angles of 98° with respect to the central naphthalene unit in the centrosymmetric *meso* form and at angles of 106 and 93° in the DL-isomer (Anton, Adam, Wagner, Qi-Lin & Müllen, 1993). The twisting of the ferrocene moieties found in the title compound is similar to that observed for the more sterically crowded 1,8-diferrocenylnaphthalene (Lee, Foxman & Rosenblum, 1985) and its ruthenium analogue (Arnold, Foxman, Rosenblum & Euler, 1988), but the severe distortions of the naphthalene moiety observed in these compounds are not displayed here. Furthermore, the displacement of the C6 atom, which links the cyclopentadiene ring to the naphthalene, from the naphthalene ring plane is only 0.021 (9) Å compared with values in excess of 0.07 Å in the 1,8-substituted complex. Despite these observations, the C6—C12 bond length of 1.495 (5) Å compares well with the values obtained for the 1,8-ferrocene and ruthenocene analogues. Bond lengths and angles within the naphthalene and ferrocenyl moieties are unremarkable, as is the angle of 1.0 (2)° between the cyclopentadienyl ring planes. The cyclopentadiene rings are approximately eclipsed with a mean C*n*—C*g*1—C*g*2—C*m* torsion angle of −6.3 (2)° (C*g*1 and C*g*2 are the centroids of the cyclopentadienyl rings, *n* = 1–5 when *m* = 7–10, 6).
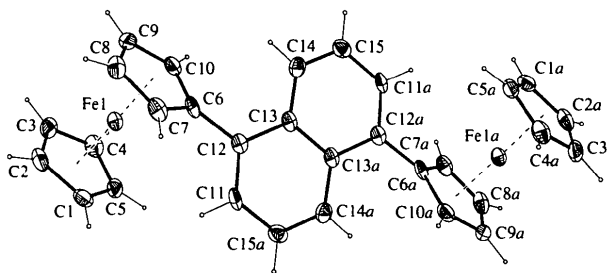

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title molecule showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

Experimental

The title compound was obtained by the Pd(dppf)Cl$_2$-catalyzed coupling of 1,5-diiodonaphthalene and ferrocenyl zinc chloride (Lee, Foxman & Rosenblum, 1985). Following separation by column chromatography (SiO$_2$/hexane), the product was crystallized from CH$_2$Cl$_2$ layered with hexane. Analysis calculated for C$_{30}$H$_{24}$Fe$_2$: C 72.62, H 4.88%; found C 72.32, H 4.65%. ^{1}H NMR (CDCl$_3$): δ 4.21 (*s*, 10H, C$_5$H$_5$), 4.40 (*t*, $^3J_{HH}$ = 1.8 Hz, 4H, C$_5$H$_4$), 4.64 (*t*, $^3J_{HH}$ = 1.8 Hz, 4H, C$_5$H$_4$),

7.43 (*m*, 2H, naphthalene), 7.9 (*m*, 2H, naphthalene), 8.4 (*m*, 2H, naphthalene).

Crystal data

[Fe$_2$(C$_5$H$_5$)$_2$(C$_{20}$H$_{14}$)]
M_r = 496.19
Monoclinic
$P2_1/n$
a = 9.657 (4) Å
b = 10.749 (3) Å
c = 10.996 (3) Å
β = 110.44 (3)°
V = 1069.6 (6) Å^3
Z = 2
D_x = 1.541 Mg m^{-3}
D_m not measured

Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 14 reflections
θ = 5.22–12.39°
μ = 1.373 mm^{-1}
T = 166 (2) K
Rhombic
0.60 × 0.45 × 0.30 mm
Orange

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction:
  ψ scans (*SHELXTL-Plus*; Sheldrick, 1990)
  T_{min} = 0.380, T_{max} = 0.419
2366 measured reflections
1871 independent reflections
1366 observed reflections
  [$I > 2\sigma(I)$]

R_{int} = 0.0271
θ_{max} = 24.99°
h = $-11 \rightarrow 2$
k = $0 \rightarrow 12$
l = $-12 \rightarrow 12$
3 standard reflections
  monitored every 97 reflections
  intensity decay: 1.31%

Refinement

Refinement on F^2
$R(F)$ = 0.0382
$wR(F^2)$ = 0.0892
S = 0.901
1871 reflections
145 parameters
H atoms refined using *HFIX* in *SHELXL*93 (Sheldrick, 1993)

$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.401 e Å^{-3}
$\Delta\rho_{min}$ = -0.322 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 ($\mathring{A}^2$)*

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

	x	*y*	*z*	U_{eq}
Fe1	0.01900 (5)	0.64381 (5)	0.29416 (5)	0.0180 (2)
C1	0.0633 (4)	0.4888 (3)	0.2078 (3)	0.0245 (8)
C2	0.0506 (4)	0.4573 (3)	0.3282 (3)	0.0266 (9)
C3	−0.0922 (4)	0.4919 (3)	0.3235 (3)	0.0264 (9)
C4	−0.1688 (4)	0.5449 (3)	0.1996 (3)	0.0256 (8)
C5	−0.0731 (4)	0.5425 (3)	0.1279 (3)	0.0243 (8)
C6	0.0692 (4)	0.8169 (3)	0.2425 (3)	0.0195 (8)
C7	0.1958 (4)	0.7590 (3)	0.3324 (3)	0.0236 (8)
C8	0.1676 (4)	0.7337 (3)	0.4471 (3)	0.0257 (9)
C9	0.0230 (4)	0.7739 (3)	0.4295 (3)	0.0240 (8)
C10	−0.0385 (4)	0.8244 (3)	0.3034 (3)	0.0238 (8)
C11	0.1051 (4)	0.7834 (3)	0.0317 (3)	0.0212 (8)
C12	0.0581 (3)	0.8596 (3)	0.1100 (3)	0.0181 (7)
C13	0.0040 (4)	0.9814 (3)	0.0643 (3)	0.0186 (8)
C14	−0.0409 (4)	1.0675 (3)	0.1399 (3)	0.0220 (8)
C15	−0.0969 (4)	1.1807 (3)	0.0928 (3)	0.0237 (8)

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

Fe1—C1	2.036 (4)	C3—C4	1.423 (5)
Fe1—C2	2.043 (4)	C4—C5	1.408 (5)
Fe1—C3	2.041 (4)	C6—C7	1.419 (5)
Fe1—C4	2.045 (4)	C6—C10	1.422 (5)
Fe1—C5	2.046 (3)	C6—C12	1.495 (5)
Fe1—C6	2.052 (3)	C7—C8	1.407 (5)
Fe1—C7	2.031 (3)	C8—C9	1.409 (5)
Fe1—C9	2.033 (3)	C9—C10	1.413 (5)
Fe1—C8	2.033 (4)	C11—C12	1.376 (5)
Fe1—C10	2.032 (3)	C11—C15^i	1.398 (5)
Fe1—*Cg*1†	1.649	C12—C13	1.435 (5)
Fe1—*Cg*2†	1.643	C13—C14	1.410 (5)
C1—C2	1.412 (5)	C13—C13^i	1.445 (6)
C1—C5	1.425 (5)	C14—C15	1.359 (5)
C2—C3	1.412 (5)	C15—C11^i	1.398 (5)
*Cg*1—Fe1—*Cg*2†	179.5	C8—C9—C10	108.0 (3)
C2—C1—C5	108.1 (3)	C9—C10—C6	108.3 (3)
C1—C2—C3	107.8 (3)	C12—C11—C15^i	122.1 (3)
C2—C3—C4	108.3 (3)	C11—C12—C13	118.9 (3)
C5—C4—C3	107.8 (3)	C11—C12—C6	120.0 (3)
C4—C5—C1	108.0 (3)	C13—C12—C6	121.0 (3)
C7—C6—C10	106.9 (3)	C14—C13—C12	122.8 (3)
C7—C6—C12	124.4 (3)	C14—C13—C13^i	118.2 (4)
C10—C6—C12	128.7 (3)	C12—C13—C13^i	118.9 (4)
C8—C7—C6	108.7 (3)	C15—C14—C13	121.8 (3)
C9—C8—C7	108.1 (3)	C14—C15—C11^i	119.9 (3)

Symmetry code: (i) $-x, 2 - y, -z$.

† *Cg*1 and *Cg*2 are the centroids of the C1–C5 and C6–C10 rings, respectively.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson 1965).

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Cyanobis(1,10-phenanthroline-N,N')-copper(II) Isothiocyanate–Phenanthroline–Water (2/1/5.5)

Ivan Potočňák, Michal Dunaj-Jurčo and Dušan Mikloš

Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia. E-mail: potocnak@cvtstu.cvt.stuba.sk

Abstract

The crystal structure of the title complex, [Cu(CN)-$(C_{12}H_8N_2)_2]_2(NCS)_2.C_{12}H_8N_2.5.5H_2O$, consists of discrete $[Cu(CN)(phen)_2]^+$ cations (phen is 1,10-phenanthroline), NCS^- anions and uncoordinated phen and water molecules. The two symmetrically independent Cu atoms are coordinated by four N atoms (from two phen molecules) and by one C atom (from the cyanide group) in the form of a distorted trigonal bipyramid (the C atom is in the equatorial plane).

Comment

The title compound, (I), was prepared and its crystal structure solved as part of a study concerning the changes in shape of the $[CuX(phen)_2]^+$ cation (X^- is a pseudo-halide anion) caused by alteration of the out-of-sphere anion.

(I)
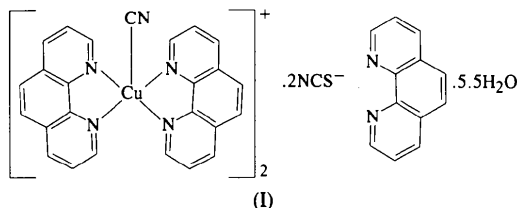
The two $[Cu(CN)(phen)_2]^+$ cations are shown in Fig. 1 with the atomic labelling, and the asymmetric part of the structure is shown in Fig. 2. The two symmetrically-independent Cu atoms are coordinated by four N atoms from the two phen molecules and by a C atom from the CN^- group, creating a CuN_4C chromophore. The coordination polyhedra are

in the form of a distorted trigonal bipyramid with the cyano C atom in the equatorial plane. The NCS^- anions, the water molecules and the remaining phen molecule do not enter the inner coordination sphere. The same $[Cu(CN)(phen)_2]^+$ cation has been found in the structures of the $[Cu(phen)_2(CN)]NO_3.H_2O$ (Anderson, 1975), $[Cu^{II}(phen)_2(CN)][Cu^I(phen)_2(CN)_2].5H_2O$ (Dunaj-Jurčo, Potočňák, Cíbik, Kabešová, Kettmann & Mikloš, 1993) and $[Cu(phen)_2(CN)][C(CN)_3].2H_2O$ (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996) complexes. The two out-of-plane Cu—N bonds in the first coordination polyhedron (Cu1—N11 and Cu1—N13) are practically of the same length [average 2.008 (4) Å] and are almost collinear [N11—Cu1—N13 170.8 (3)]. The two in-plane Cu—N bonds (Cu1—N12 and Cu1—N14) are significantly different in length [2.085 (6) and 2.129 (6) Å, respectively] and their mean is longer by 0.099 Å than the mean of the out-of-plane Cu1—N distances. The third in-plane bond [Cu1—C1 1.948 (8) Å] is significantly shorter than the other two Cu—N in-plane bonds. The out-of-plane angles lie within the range 80.2 (2)–96.2 (3)°.

Similar features are observed in the geometry of the second coordination polyhedron. The out-of-plane Cu—N bonds (Cu2—N21 and Cu2—N23) average 2.006 (6) Å and the angle between them is 169.7 (3)°. The two in-plane Cu—N bonds (Cu2—N22 and Cu2—
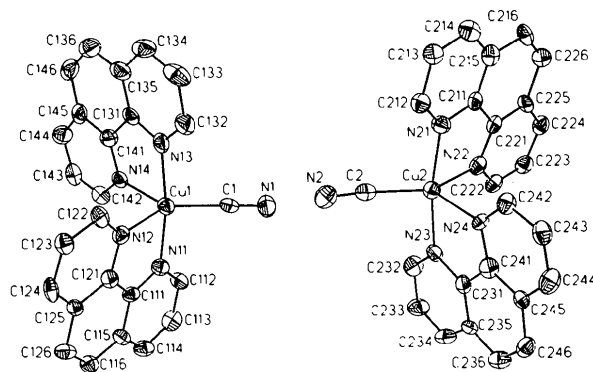

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the cations showing the atom labelling. Displacement ellipsoids are plotted at the 40% probability level.
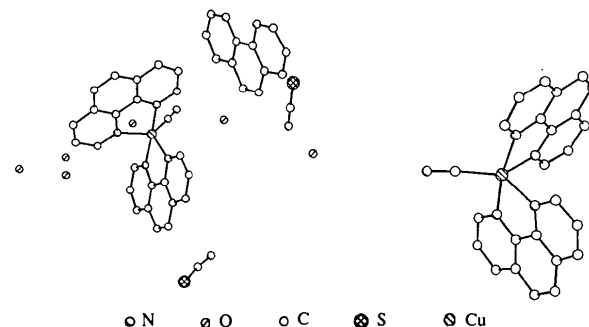

Fig. 2. The asymmetric part of the title structure.