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*Acta Cryst.* (1996). **C52**, 2414–2416

## Bis( $\eta^5$ -hydropentalenyl)iron

ELIES MOLINS,<sup>a</sup> WALDEMAR MANTUKIEWICZ,<sup>a</sup> CARLOS MIRAVITLLES,<sup>a</sup> MONTSE MAS,<sup>a</sup> JUAN M. MANRIQUEZ,<sup>b</sup> IVONNE CHAVEZ,<sup>c</sup> BEATRIZ OELCKERS,<sup>d</sup> JOAN FARRAN<sup>e</sup> AND JOSÉ LUIS BRIANSÓ<sup>e</sup>

<sup>a</sup>Institut de Ciència de Materials de Barcelona, Campus UAB, 08193 Bellaterra, Spain, <sup>b</sup>Centro de Investigación Minera y Metalúrgica, Avda. Parque A. Rabat 6500, Santiago, Chile, <sup>c</sup>Departamento de Ciencias de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 307, Santiago, Chile, <sup>d</sup>Instituto de Química, Universidad Católica de Valparaíso, Avda. Brasil 2950, Valparaíso, Chile, and <sup>e</sup>Unidad de Cristalografía, Universidad Autónoma de Barcelona, 08193 Bellaterra, Spain. E-mail: elies.molins@icmab.es

(Received 7 February 1996; accepted 7 May 1996)

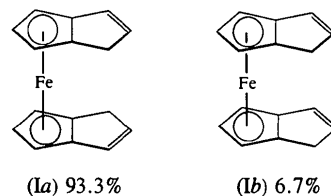
### Abstract

In the structure of bis[(3a,4,5,6,6a- $\eta$ )-1-hydropentalenyl]iron,  $[Fe(C_8H_7)_2]$ , the two pentalene ligands are parallel. The molecules are packed in chains along the *a* axis and there are no significant intermolecular interactions. The compound shows disorder at the iron position with a 93.3% major and a 6.7% minor component. The structure of the predominant component has been determined. In addition, the double bond in one pentalene ligand is disordered. This confirms the results of a previous spectroscopic <sup>1</sup>H NMR study [Katz & Rosenberger (1963). *J. Am. Chem. Soc.* **85**, 2030–2031].

### Comment

The title compound, (I), has been used recently as a useful building block in the synthesis of triple- and quadruple-decker pentalene complexes (Oelckers, Chávez, Manríquez & Román, 1993). The present structure is the first single crystal X-ray study of a dihydropentalenyl–metal complex. The only other related structure is that of (1,1'-dihydro-1,1'-bipentalenyl)iron,

where the 'ferrocene' moiety is distorted due to the dimerization of the two pentalene ligands via 1-*endo*,1'-*endo* C—C bond formation (Churchill & Lin, 1973).



An ORTEP (Johnson, 1965) drawing of (I) is shown in Fig. 1. The Fe—C distances of 2.035 (2)–2.068 (2) Å are similar to those found for ferrocene (Seiler & Dunitz, 1979). The two planar five-membered rings are tilted 1.24 (11)° from being parallel and twisted ca 0.5 (2)° (mean) from an eclipsed conformation. The C—C distances (mean) within the  $\pi$ -cyclopentadienyl rings range from 1.416 (3) to 1.434 (3) Å [average 1.422 (3) Å].

In the crystal, the complex molecules are packed in chains (Fig. 2), with the intermolecular separation within a chain exceeding 3.5 Å.

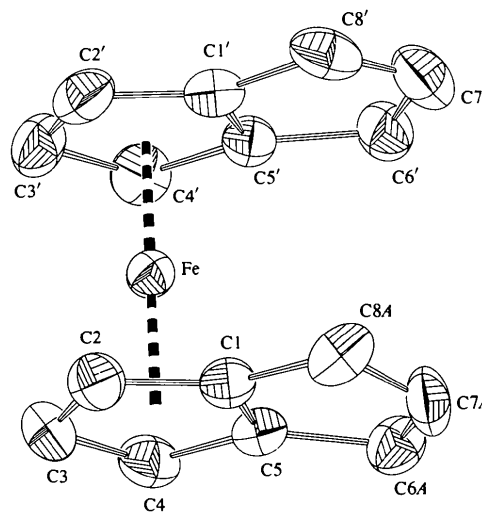


Fig. 1. View of the title structure showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted.

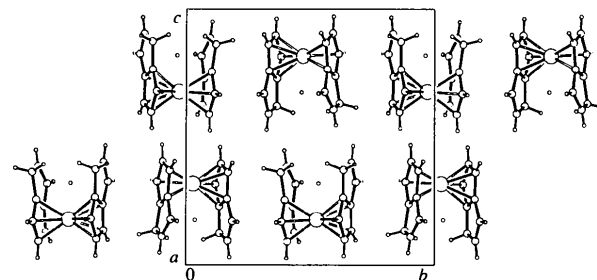


Fig. 2. Projection of the title structure down the *a* axis. The non-bonded small circles represent the positions of the Fe' atoms.

## Experimental

The title compound was prepared according to the procedure described previously by Katz & Rosenberger (1963). Crystals suitable for X-ray analysis were obtained after sublimation (353 K,  $1.3 \times 10^{-1}$  Pa).

### Crystal data

[Fe(C<sub>8</sub>H<sub>7</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 262.12  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 6.080 (2) Å  
*b* = 13.552 (4) Å  
*c* = 13.882 (7) Å  
 $\beta$  = 96.62 (2)°  
*V* = 1136.2 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.532 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.7107 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 11.92–27.97°  
 $\mu$  = 1.297 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism  
 0.72 × 0.60 × 0.50 mm  
 Dark red

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan (North, Phillips & Mathews, 1968)  
*T<sub>min</sub>* = 0.84, *T<sub>max</sub>* = 0.99  
 3704 measured reflections  
 3433 independent reflections

2701 observed reflections [*I* > 2σ(*I*)]  
*R<sub>int</sub>* = 0.023  
 $\theta_{\max}$  = 30.32°  
*h* = 0 → 8  
*k* = 0 → 19  
*l* = -19 → 19  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 0.5%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.0303  
 $wR(F^2)$  = 0.0810  
*S* = 1.005  
 3166 reflections  
 191 parameters  
 H atoms treated using a riding model  
 $w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.3366P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = -0.008  
 $\Delta\rho_{\max}$  = 0.377 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.312 e Å<sup>-3</sup>  
 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<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Fe†	0.22780 (4)	0.02838 (2)	0.31986 (2)	0.0283 (1)
Fe'‡	0.2799 (5)	0.0357 (3)	0.1784 (2)	0.0324 (11)
C1†	0.4451 (3)	-0.07070 (12)	0.26845 (11)	0.0330 (4)
C1'‡	0.2810 (3)	0.16550 (12)	0.26151 (13)	0.0361 (5)
C2†	0.4832 (3)	-0.06369 (14)	0.37131 (13)	0.0403 (5)
C2'‡	0.3174 (3)	0.16894 (13)	0.36417 (14)	0.0433 (6)
C3†	0.2822 (3)	-0.09212 (14)	0.40717 (13)	0.0445 (5)
C3'‡	0.1161 (3)	0.14071 (15)	0.39846 (14)	0.0461 (6)
C4†	0.1205 (3)	-0.11518 (13)	0.32797 (13)	0.0405 (5)
C4'‡	-0.0456 (3)	0.11807 (14)	0.31799 (13)	0.0409 (5)
C5†	0.2237 (3)	-0.10211 (11)	0.24239 (11)	0.0336 (4)
C5'‡	0.0601 (3)	0.13407 (12)	0.23317 (12)	0.0327 (4)

C6'†	0.0175 (3)	0.13539 (15)	0.12519 (13)	0.0431 (5)
C6A‡	0.173 (2)	-0.1188 (16)	0.1356 (3)	0.040 (2)
C6B‡	0.200 (2)	-0.1112 (14)	0.1359 (2)	0.040 (2)
C7'†	0.2297 (4)	0.16781 (16)	0.09600 (15)	0.0531 (7)
C7A‡	0.398 (2)	-0.0950 (10)	0.1120 (8)	0.053 (3)
C7B‡	0.3833 (18)	-0.0828 (9)	0.0944 (8)	0.0380 (17)
C8'†	0.3850 (3)	0.18602 (14)	0.17338 (16)	0.0468 (6)
C8A‡	0.5575 (13)	-0.0594 (10)	0.1806 (4)	0.043 (3)
C8B‡	0.5533 (15)	-0.0644 (10)	0.1774 (4)	0.045 (4)

† Site occupancy = 0.933 (1). ‡ Site occupancy = 0.067 (1). § Site occupancy = 0.466 (1).

Table 2. Selected geometric parameters (Å, °)

Fe—C1	2.068 (2)	C1'—C5'	1.421 (3)
Fe—C1'	2.067 (2)	C1'—C2'	1.418 (3)
Fe—C2	2.055 (2)	C2—C3	1.425 (3)
Fe—C2'	2.056 (2)	C2'—C3'	1.416 (3)
Fe—C3	2.038 (2)	C3—C4	1.423 (3)
Fe—C3'	2.035 (2)	C3'—C4'	1.434 (3)
Fe—C4	2.059 (2)	C4—C5	1.417 (3)
Fe—C4'	2.057 (2)	C4'—C5'	1.422 (3)
Fe—C5	2.068 (2)	C5'—C6'	1.492 (3)
Fe—C5'	2.063 (2)	C6'—C7'	1.464 (3)
C1—C2	1.423 (2)	C7'—C8'	1.368 (3)
C1'—C8'	1.467 (3)		
C1—Fe—C1'	108.26 (7)	C3—Fe—C3'	108.78 (8)
C1—Fe—C2	40.39 (7)	C3—Fe—C4	40.63 (8)
C1—Fe—C5	40.11 (7)	C3'—Fe—C4'	41.02 (8)
C1'—Fe—C2'	40.21 (8)	C4—Fe—C4'	107.36 (8)
C1'—Fe—C5'	40.23 (7)	C4—Fe—C5	40.16 (7)
C2—Fe—C2'	107.16 (8)	C4'—Fe—C5'	40.37 (7)
C2—Fe—C3	40.74 (8)	C5—Fe—C5'	108.35 (7)
C2'—Fe—C3'	40.50 (8)		

The structure of the title compound was solved by Patterson and difference Fourier methods. Refinement was based on full-matrix least squares with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms. All H atoms were included at calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2*U<sub>eq</sub>* of the attached C atom. After initial refinement, a significant electron-density peak remote from the other atoms was noted in the  $\Delta F$  map. This peak was interpreted as originating from the Fe' atom of a disordered molecule. The site-occupancy factor of the two Fe-atom positions was refined as an additional variable by constraining the sum of the two values to 1. Due to the very unequal ratio of the molecules in the crystal, we were only able to determine the structure of the major component. Then, during the course of refinement of this model, we observed olefinic bond lengths in one of the five-membered rings [C6—C7 1.418 (3) and C7—C8 1.427 (3) Å]. In comparison, the C7'=C8' double bond length is 1.368 (3) Å. This elongation indicates the presence of a 50:50 mixture of double-bond isomers in the crystal and was consistent with the <sup>1</sup>H NMR spectrum of the compound, where the presence of two peaks in the allylic region was observed. The disordered five-membered ring was modelled by splitting the C6, C7 and C8 positions in order to make it similar to its equivalent ordered ring from the other pentalene system.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1995a) and *PLUTON* (Spek, 1995b). Software used to prepare material for publication: *PLATON*.

Financial support was provided by CEE grant CH1\*CT91-0913, FONDECYT grant 1930024, DICYT grant 02-9542CHM and DGICYT grant PB92-0594.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1230). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1996). **C52**, 2416–2419

## Silver(I) Complexes of 1,4-Dicyanobenzene

D. VENKATARAMAN,<sup>a</sup> GEOFFREY B. GARDNER,<sup>b</sup> AARON C. COVEY,<sup>b</sup> STEPHEN LEE<sup>b</sup> AND JEFFREY S. MOORE<sup>c</sup>

<sup>a</sup>Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801, USA,

<sup>b</sup>Department of Chemistry, Willard H. Dow Laboratory, University of Michigan, Ann Arbor, Michigan 48109-1055, USA, and <sup>c</sup>Departments of Chemistry and Materials Science & Engineering, University of Illinois, Urbana, Illinois 61801, USA. E-mail: moore@aries.scs.uiuc.edu

(Received 14 August 1995; accepted 13 May 1996)

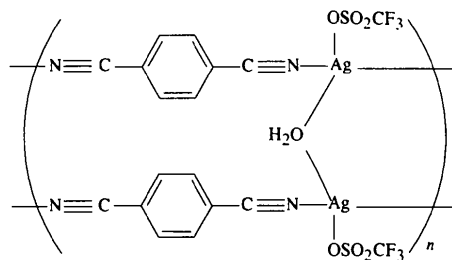
### Abstract

The crystal structures of the complexes of 1,4-benzenedinitrile with silver(I) trifluoromethanesulfonate, *catena*-poly[ $\{\mu$ -(*aqua-O,O*)-bis[(trifluoromethanesulfonato-*O*)]silver(I)]-di- $\mu$ -(1,4-benzenedinitrile-*N:N'*)], [Ag<sub>2</sub>(CF<sub>3</sub>O<sub>3</sub>S)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sub>n</sub>, and *catena*-poly[[di-

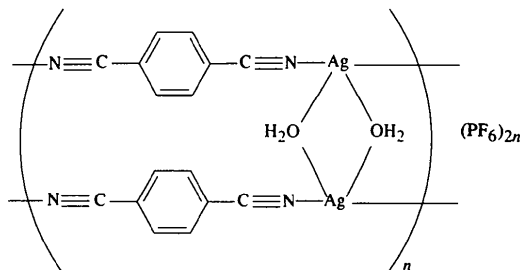
$\mu$ -(*aqua-O,O*)-disilver(I)]- $\mu$ -(1,4-benzenedinitrile-*N:N'*) bis(hexafluorophosphate)], [Ag<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>(PF<sub>6</sub>)<sub>2n</sub>, show that irrespective of the counterion, the basic network formed is that of a chain structure. Water molecules located in the unit cell of these structures bridge a pair of adjacent chains by coordinating to silver(I) resulting in ladder-type motifs.

### Comment

The use of coordination bonds in the construction of supramolecular networks has received much attention (Carlucci, Ciani, Proserpio & Sironi, 1995; Fujita, Kwon, Washizu & Ogura, 1994; Gardner, Venkataraman, Moore & Lee, 1995; Hoskins & Robson, 1990; Moore & Lee, 1994; Yaghi & Li, 1995). As part of a continuing study on the use of Ag—N bonds for the construction of coordination networks, we were interested in the role of the counterion on the final network motif and hence crystallized the 1,4-dicyanobenzene.AgOTf, (1) (OTf is trifluoromethanesulfonate), and 1,4-dicyanobenzene.AgPF<sub>6</sub>, (2), complexes. The basic network in these structures is a one-dimensional chain. Water molecules located in the unit cell bridge a pair of adjacent chains by coordinating to silver(I), forming ladder-type motifs.



(1)



(2)

In the structure of 1,4-dicyanobenzene.AgOTf, (1), silver(I) is four-coordinate and adopts a trigonal pyramidal geometry (Fig. 1). Two nitrile groups of 1,4-dicyanobenzene and an O atom of a water molecule are in the basal plane, with the apical position occupied by an O atom of the trifluoromethanesulfonate anion. The O atom of the water molecule lies on