During a first data collection, the intensities of the two standards increased by a total of about 100%. This was taken to indicate a transformation of the crystal in the X-ray beam towards the ideally imperfect state. When the intensities seemed stable, a second data collection was started. This second data set, with only 1.6% intensity decrease, was used for the structure determination. The Laue group is $4/m$ and systematic extinctions (hkl: $h + k + l \neq 2n$; $hk0$: $h \neq 2n$; $00l$: $l \neq 4n$) are consistent with the space group $I4_1/a$ (No. 88), which was verified by the statistical analysis of intensity distribution, packing considerations and the successful refinement of the structure.

Data collection: local diffractometer control program. Cell refinement: *LATCON* in *XRAY76* (Stewart *et al.*, 1976). Data reduction: *TEXSAN PREPROCESS* and *PROCESS* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *TEXSAN MITHRIL*. Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bailey, R. D. & Pennington, W. T. (1995). *Acta Cryst.* C**51**, 226–229.
Bengtsson, L. A., Norén, B. & Stegemann, H. (1995). *Acta Chem. Scand.* **49**, 391–398.
Bu, X., Su, Z. & Coppens, P. (1991). *Acta Cryst.* C**47**, 279–282.
Gritsenko, V. V., Konovalikhin, S. V., D'yachenko, O. A., Lyubovskaya, R. N. & Zhilyaeva, E. I. (1990). *Izv. Akad. Nauk SSSR Ser. Khim.* **1**, 2773–2777.
Kallel, A., Bats, J. W. & Daoud, A. (1981). *Acta Cryst.* B**37**, 676–677.
Kallel, A., Borg, M., Fuess, H. & Boutiba, S. (1991). *Phase Transit.* **33**, 115–118.
Leemput, P. J. H. A. M. van der, Cras, J. A. & Willemse, J. (1977). *Rec. Trav. Chim. Pays-Bas*, **96**, 288–292.
Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software.* Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nieuwenhuyzen, M., Robinson, W. T. & Wilkins, C. J. (1991). *Polyhedron*, **10**, 2111–2121.
Nieuwenhuyzen, M., Wen, H. & Wilkins, C. J. (1992). *Z. Anorg. Allg. Chem.* **615**, 143–148.
Ohtaki, H., Maeda, M. & Ito, S. (1974). *Bull. Chem. Soc. Jpn*, **47**, 2217–2221.
Orioli, P. L. & Ciampolini, M. (1972). *J. Chem. Soc. Chem. Commun.* pp. 1280–1281.
Pocev, S., Triolo, R. & Johansson, G. (1979). *Acta Chem. Scand.* **33**, 179–185.
Rogers, R. D., Bond, A. H., Aguinaga, S. & Reyes, A. (1993). *Inorg. Chim. Acta*, **212**, 225–231.
Sjövall, R. (1989). *Acta Cryst.* C**45**, 667–669.
Sjövall, R., Svensson, C. & Lidin, S. (1996). *Z. Kristallogr.* **211**, 234–237.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System.* Technical Report TR-446. Computer Science Center, University of Maryland, College Park, Maryland, USA.
Thiele, G. & Putzas, D. (1988). *Z. Naturforsch. Teil B*, **43**, 1224–1228.

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Triple-Decker Pentalene Complex of Iron and Cobalt

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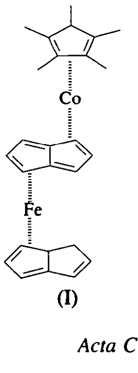
Abstract

In [1(1,2,3,3a,6a-η)-1,4-dihydropentalenyl][μ-1(1,2,3,3a,-6a-η):2(3a,4,5,6,6a-η)-pentalene][2(η^5)-pentamethylcyclopentadienyl]cobaltiron, [$CoFe(C_8H_7)Cp^*(C_8H_6)$] ($Cp^* = C_{10}H_{15}$), the Cp*–Co and (C_8H_7)–Fe moieties reside on opposite sides of the fused bridging pentalene ring system.

Comment

Model sandwich complexes having two or more metals, which may be considered as the smallest segments of one-dimensional conducting materials, are excellent candidates for the detailed study of metal–metal interactions. We have recently developed a systematic controlled route for the preparation of triple- and quadruple-decker molecular-sandwich derivatives of pentalene (Oelckers, Chávez, Manríquez & Román, 1993). As a part of this general study, we present here the structure of the title compound, (I), which may serve as a potential building block in the preparation of larger polymetallic systems.



(I)

The intramolecular Co$\cdots$Fe distance in (I) (Fig. 1), which may be useful when modelling high polymers, is 4.149 (3) Å. The two rings associated with the Co and Fe atoms are slightly tilted from being parallel. The dihedral angles between the mean planes of these rings are 1.8 (3) and 4.6 (3)°, respectively. The metal–ring distances vary appreciably, being 1.700 (2) and 1.763 (2) Å for Co, and 1.668 (2) and 1.652 (2) Å for Fe.

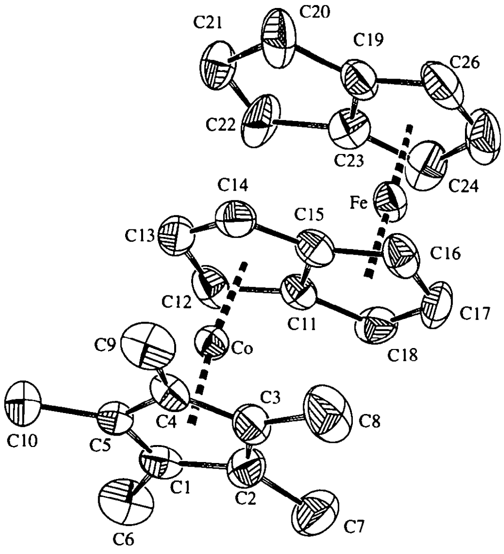


Fig. 1. View of (I) showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

There is a difference in the position of the metal atoms with respect to the central pentalene ring system. The Co atom is located away from the centre of the associated five-membered ring of the bridging pentalene system, whereas the Fe atom is located near the centre of its associated five-membered ring moiety. The 'ring slippage' (*i.e.* the distance between perpendicular projection of a heavy-atom position on the least-squares plane of the ring and the ring centre) is 0.277 Å for Co and 0.083 Å for Fe. This may arise from the differences in the electronic configuration of the two metals, *e.g.* the Co atom would form a more stable complex by binding to the pentalene ligand in a η^4 rather than a η^5 manner. This is confirmed by the non-planarity of the five-membered ring of the bridging pentalene connected to the Co atom. This ring is slightly distorted from planarity [puckering parameters (Cremer & Pople, 1975): Q = 0.095 (5) Å and φ = 268.5 (3)°], while the second ring of the bridging pentalene system, as well as the other five-membered rings connected to Fe or Co, are planar (within a 4σ range). Furthermore, the fused rings of the central pentalene ligand are not fully coplanar and form a dihedral angle of 1.3 (3)° with respect to one another. Each pair of five-membered rings in the Co and Fe moieties are nearly eclipsed, with average staggered angles of 6.0 (4) and 4.6 (4)°, respectively. In the terminal pentalene ligand, we observe disorder due to 1:1 double-bond isomers.

Experimental

The title compound, (I), was prepared according to the method of Oelckers, Chávez, Manríquez & Román (1993). Good quality crystals were grown by slow evaporation of a solution of the complex in diethyl ether.

Crystal data

[CoFe(C_8H_7)($C_{10}H_{15}$)(C_8H_6)]
M_r = 455.29
Orthorhombic
$P2_12_12_1$
a = 10.745 (1) Å
b = 13.546 (2) Å
c = 14.300 (2) Å
V = 2081.4 (5) Å^3
Z = 4
D_x = 1.453 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 17.56–27.23°
μ = 1.502 mm^{-1}
T = 294 (2) K
Prism
0.50 × 0.25 × 0.20 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.70, $T_{\max}$ = 0.74
3547 measured reflections
3522 independent reflections

1797 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max}$ = 30.39°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: 7.0%

Refinement

Refinement on F^2
$R(F)$ = 0.0335
$wR(F^2)$ = 0.0644
S = 1.116
3522 reflections
288 parameters
H atoms treated using a riding model
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.032

$\Delta\rho_{\max}$ = 0.306 e Å^{-3}
$\Delta\rho_{\min}$ = −0.328 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)
Absolute configuration: Flack (1983)
Flack parameter = −0.04 (3)

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	$U_{\rm eq}$
Co	−0.01867 (5)	−0.08039 (4)	0.52101 (4)	0.0335 (2)
Fe	0.23529 (6)	0.10151 (4)	0.38651 (4)	0.0376 (2)
C1	−0.2103 (4)	−0.0917 (3)	0.5324 (3)	0.0397 (14)
C2	−0.1712 (4)	−0.1165 (3)	0.4384 (3)	0.0433 (16)
C3	−0.0910 (5)	−0.1976 (4)	0.4448 (3)	0.0433 (17)
C4	−0.0806 (4)	−0.2242 (3)	0.5424 (3)	0.0390 (14)
C5	−0.1572 (4)	−0.1611 (3)	0.5940 (3)	0.0350 (14)

C6	−0.2994 (4)	−0.0120 (3)	0.5589 (4)	0.0603 (19)
C7	−0.2112 (5)	−0.0645 (4)	0.3508 (4)	0.069 (2)
C8	−0.0278 (5)	−0.2492 (4)	0.3651 (4)	0.079 (2)
C9	−0.0062 (5)	−0.3104 (3)	0.5790 (4)	0.0617 (19)
C10	−0.1809 (5)	−0.1630 (4)	0.6980 (3)	0.0590 (19)
C11	0.0704 (4)	0.0528 (3)	0.4505 (3)	0.0330 (14)
C12	0.0319 (4)	0.0631 (3)	0.5470 (3)	0.0443 (16)
C13	0.1033 (4)	−0.0035 (3)	0.6004 (3)	0.0473 (17)
C14	0.1701 (4)	−0.0675 (4)	0.5404 (3)	0.0430 (16)
C15	0.1585 (4)	−0.0282 (3)	0.4461 (3)	0.0387 (14)
C16	0.1920 (4)	−0.0408 (3)	0.3504 (3)	0.0443 (17)
C17	0.1241 (5)	0.0280 (3)	0.2974 (3)	0.0510 (16)
C18	0.0518 (4)	0.0874 (3)	0.3570 (3)	0.0443 (17)
C19	0.3858 (5)	0.1455 (3)	0.4647 (3)	0.0457 (17)
C20†	0.409 (2)	0.1248 (19)	0.5653 (7)	0.075 (10)
C20′†	0.4075 (14)	0.1190 (15)	0.5633 (8)	0.048 (8)
C21†	0.328 (3)	0.1853 (18)	0.6232 (18)	0.046 (7)
C21′†	0.325 (3)	0.181 (2)	0.6091 (19)	0.068 (9)
C22†	0.259 (2)	0.2387 (19)	0.5596 (7)	0.057 (8)
C22′†	0.2564 (17)	0.253 (2)	0.5554 (8)	0.039 (6)
C23	0.2951 (4)	0.2226 (3)	0.4607 (3)	0.0413 (16)
C24	0.2743 (5)	0.2477 (3)	0.3664 (3)	0.0537 (18)
C25	0.3564 (6)	0.1860 (4)	0.3128 (4)	0.066 (2)
C26	0.4237 (5)	0.1222 (4)	0.3723 (4)	0.060 (2)

† Site occupancy = 0.50.

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

Co—C13	2.023 (4)	Fe—C17	2.011 (5)
Co—C12	2.052 (4)	Fe—C18	2.026 (4)
Co—C14	2.054 (4)	Fe—C25	2.029 (5)
Co—C1	2.071 (4)	Fe—C24	2.044 (4)
Co—C3	2.077 (5)	Fe—C16	2.049 (4)
Co—C2	2.078 (5)	Fe—C26	2.054 (5)
Co—C4	2.081 (4)	Fe—C19	2.055 (5)
Co—C5	2.122 (4)	Fe—C23	2.056 (4)
Co—C11	2.278 (4)	Fe—C11	2.100 (4)
Co—C15	2.296 (4)	Fe—C15	2.120 (4)
C12—Co—C1	108.6 (2)	C17—Fe—C25	109.4 (2)
C14—Co—C4	112.1 (2)	C18—Fe—C24	105.2 (2)
C13—Co—C5	116.3 (2)	C16—Fe—C26	109.1 (2)
C2—Co—C11	105.4 (2)	C23—Fe—C11	106.8 (2)
C3—Co—C15	107.5 (2)	C19—Fe—C15	109.1 (2)

The Co- and Fe-atom positions were determined by the Patterson method and the remaining non-H atoms were found from $\Delta\rho$ maps. The assignment of the heavy atoms as Co and Fe was performed using the different chemical environments known from the synthetic work. All H atoms were included at calculated positions and refined using a riding model, with isotropic displacement parameters equal to $1.2U_{\rm eq}$ of the attached C atom. The occupancies of the disordered C20–C22 atoms were not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1995). Software used to prepare material for publication: *PLATON*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1392). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1969). *Acta Cryst.* A**24**, 351–359.

Oelckers, B., Chávez, I., Manríquez, J. M. & Román, E. (1993). *Organometallics*, **12**, 3396–3397.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1995). *PLATON. Program for Analysis of Derived Crystal Structure Results*. Version of October 1995. University of Utrecht, The Netherlands.

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Restricting Chelate Ring Flipping in Cu$^{\rm II}$ Complexes. I. Non-Thermochromic Bis(*o*-phenylenediamine-*N*,*N*′)copper(II) Bis(tetrafluoroborate)

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Abstract

The title complex, $[\rm Cu(C_6H_8N_2)_2](BF_4)_2$, is the first in a series where the phenylenediamine collar restricts the 'flipping' of the chelate ring C atoms, which is the mechanism responsible for the thermochromic transition in *N*,*N*-diethylethylenediamine complexes. The Cu$^{\rm II}$ ion has tetragonally distorted octahedral geometry, with four short equatorial Cu—N bonds [2.023 (3) and 1.990 (3) Å] and two long mutually *trans* axial Cu···F interactions [2.546 (2) Å]. The features of the molecular packing, namely the shorter metal-to-anion contacts and the stronger N—H···F hydrogen bonds compared with those in the thermochromic analogues, seem to be associated with non-thermochromic behaviour.

Comment

Complexes of copper and nickel with *N*,*N*-diethylenediamine exhibit reversible first-order thermochromic phase transitions (Bloomquist & Willett, 1982). Variable-temperature single-crystal X-ray studies of [Cu(*N*,*N*-diethylethylenediamine)$_2$](ClO$_4$)$_2$ carried out by