2,6-Bis(3-ferrocenyl-5-methyl-1*H*-pyrazol-1-yl-carbonyl)pyridine

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Molecules of the title compound, $[Fe_2(C_5H_5)_2(C_{25}H_{19}N_5O_2)]$, crystallize as enantiomeric pairs, located about inversion centers, thus acting as centrosymmetric dimers.

Comment

Pyrazole and polypyrazole compounds are finding increasing applications as ligands in coordination chemistry (Chakrabarty *et al.*, 2004; Davies *et al.*, 2005; Hardie *et al.*, 2004; Michaud *et al.*, 2005; Röder *et al.*, 2004), supramolecular chemistry (Miranda *et al.*, 2005) and organometallic chemistry (Esquius *et al.*, 2001; Reger *et al.*, 1996). As part of an ongoing investigation of the chemistry of organometallic pyrazoles, the title compound, (I), was synthesized (Shi *et al.*, 2005) and its crystal structure determined (Fig. 1).

(I)
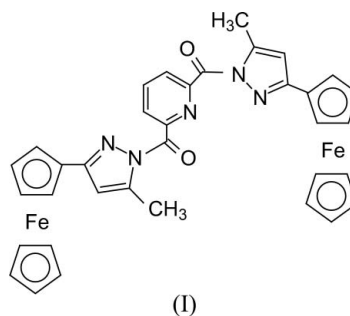
Compound (I) crystallizes in the centrosymmetric space group $P\bar{1}$. Two chiral molecules are present as an enantiomeric pair in the unit cell. For each pyrazole ring in (I), the bond distances (Table 1) are very close to those in N,N'-butane-dioylbis(5-ferrocenyl-3-methyl-1*H*-pyrazole), indicating elec-
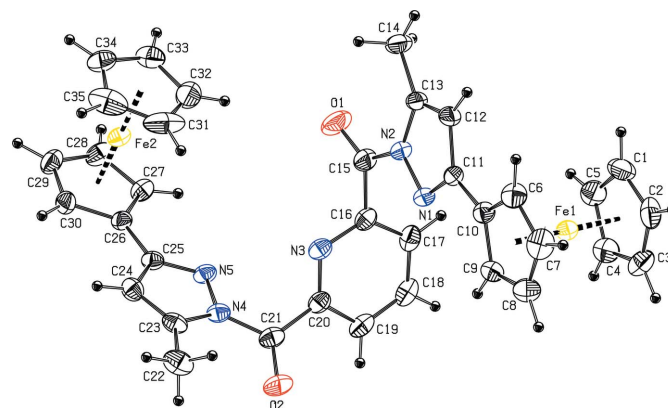
Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

tron delocalization (Gilchrist, 1997; Shi *et al.*, 2005). The dihedral angles between the pyridine ring and the two pyrazole rings (the N1/C13 ring and N4/C25 ring) are 81.7 (2) and 66.1 (2)°, respectively. The dihedral angles between the pyridine ring and the two carbonyl planes (the O1/C15/N2 and O2/C21/N4 planes) are 74.1 (5) and 42.9 (5)°, respectively. Interestingly, consistent with the large dihedral angles, the C15—C16 and C20—C21 bonds [1.508 (6) and 1.486 (6) Å] are typical of a single bond (Csp^2—Csp^2), suggesting that the carbonyl groups are not involved in conjugation with the pyridine ring. However, dihedral angles of 6.9 (2) and 1.3 (2)° between the pyrazole ring and the adjacent substituted cyclopentadienyl ring indicate that they are conjugated with each other; this is in accord with the C10—C11 and C25—C26 bonds [1.452 (5) and 1.459 (5) Å], which have double-bond character.

Aromatic π–π stacking interactions between the pyridine ring in the molecule at (x, y, z) and the corresponding ring in the molecule at $(1 - x, 1 - y, 1 - z)$ is found in the crystalline state of the title compound. The ring-centroid and interplanar distances of 3.681 (3) and 3.343 Å, respectively, show that in the unit cell two chiral molecules form a centrosymmetric dimer at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Glidewell *et al.*, 2005).

Experimental

A mixture of $SOCl_2$ (4 ml, 55 mmol) and pyridine-2,6-dicarboxylic acid (5 mmol) was refluxed under N_2 until the solid disappeared. After removal of $SOCl_2$, the residue was dissolved in 10 ml of THF and cooled to 273 K. To this solution were added dropwise Et_3N (2 ml, 14.3 mmol) in 5 ml of THF and 3-ferrocenyl-5-methyl-1*H*-pyrazole (10 mmol) in 15 ml of THF. The reaction mixture was allowed to reach ambient temperature and stirred for 20 h. The solvent was evaporated under reduced pressure and the resulting solid was purifed by chromatography on silica gel (eluant 5:1 *v*/*v*, dichloromethane–diethyl ether) to afford an orange–yellow solid (m.p. 513.6–514.4 K, yield 38.4%). Orange–red crystals of the title compound suitable for single-crystal *X*-ray diffraction were obtained from a dichloromethane/acetone solution (2:3). IR (KBr): 3101 (*m*, CH), 1711 (*s*, O=C), 1589 (*m*, C=N), 1358 (vs, C–N) cm^{-1}.

Crystal data

[Fe$_2$(C$_5$H$_5$)$_2$(C$_{25}$H$_{19}$N$_5$O$_2$)]	$V = 1478.8$ (6) Å^3
$M_r = 663.33$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.490$ Mg m^{-3}
$a = 10.483$ (2) Å	Mo $K\alpha$ radiation
$b = 11.850$ (2) Å	$\mu = 1.02$ mm^{-1}
$c = 13.033$ (3) Å	$T = 295$ K
$\alpha = 88.76$ (3)°	Block, orange–red
$\beta = 68.75$ (3)°	$0.20 \times 0.15 \times 0.10$ mm
$\gamma = 78.92$ (3)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	5788 independent reflections
$\omega/2\theta$ scans	4378 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{int} = 0.042$
$T_{min} = 0.822$, $T_{max} = 0.905$	$\theta_{max} = 26.0°$
6122 measured reflections	3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0937P)^2 + 0.1751P]$
$R[F^2 > 2\sigma(F^2)] = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.156$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.08$	$\Delta\rho_{max} = 1.04$ e Å^{-3}
5788 reflections	$\Delta\rho_{min} = -0.97$ e Å^{-3}
399 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Fe1—C1	2.031 (5)	Fe2—C26	2.026 (3)
Fe1—C2	2.034 (4)	Fe2—C27	2.035 (4)
Fe1—C3	2.036 (4)	Fe2—C28	2.041 (4)
Fe1—C4	2.038 (4)	Fe2—C29	2.039 (4)
Fe1—C5	2.022 (4)	Fe2—C30	2.023 (4)
Fe1—C6	2.034 (4)	Fe2—C31	2.017 (5)
Fe1—C7	2.037 (4)	Fe2—C32	2.020 (5)
Fe1—C8	2.037 (4)	Fe2—C33	2.039 (4)
Fe1—C9	2.031 (4)	Fe2—C34	2.034 (4)
Fe1—C10	2.028 (4)	Fe2—C35	2.020 (4)

All H atoms in (I) were placed at geometrically idealized positions and subsequently treated as riding atoms, with C—H distances of 0.93 (aromatic and olefinic) and 0.96 Å (CH$_3$), and with U_{iso}(H) values of $1.2U_{eq}$(C) or $1.5U_{eq}$(methyl C). The highest residual density peak is located 1.01 Å from atom Fe2.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo,1995); program(s) used to solve structure: *OSCAIL-X* (McArdle, 2005) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL-X* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

References

Chakrabarty, S., Poddar, R. K., Poulsen, R. D., Thompson, A. L. & Howard, J. A. K. (2004). *Acta Cryst.* C**60**, m628–m630.
Davies, G. M., Adams, H. & Ward, M. D. (2005). *Acta Cryst.* C**61**, m221–m223.
Enraf–Nonius. (1989). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
Esquius, G., Pons, J., Yáñez, R. & Ros, J. (2001). *J. Organomet. Chem.* **619**, 14–23.
Gilchrist, T. L. (1997). *Heterocyclic Chemistry*, 3rd ed. London: Addison Wesley Longman Limited.
Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* C**61**, o209–o210.
Hardie, M. J., Kilner, C. A. & Halcrow, M. A. (2004). *Acta Cryst.* C**60**, m177–m179.
Harms, K. & Wocadlo, S. (1995). *XCAD4* University of Marburg, Germany.
McArdle, P. (2005). *OSCAIL-X for Windows*. Version 1.04. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Michaud, A., Fontaine, F.-G. & Zargarian, D. (2005). *Acta Cryst.* E**61**, m904–m906.
Miranda, C., Escartí, F., Lamarque, L., García-España, E., Navarro, P., Latorre, J., Lloret, F., Jiménez, H. R. & Yunta, M. J. R. (2005). *Eur. J. Inorg. Chem.* , 189-208.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Reger, D. L., Collins, J. E., Rheingold, A. L. & Liable-Sands, L. M. (1996). *Organometallics*, **15**, 2029–2032.

Röder, J. C., Meyer, F., Kaifer, E. & Pritzkow, H. (2004). *Eur. J. Inorg. Chem.* pp. 1646–1660.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Shi, Y.-C., Sui, C.-X. & Cheng, H.-J. (2005). *Acta Cryst.* E**61**, m1563–m1565.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.