# metal-organic papers

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Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(C–C) = 0.007 Å
R factor = 0.044
wR factor = 0.171
Data-to-parameter ratio = 14.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

1,3-Bis(3-ferrocenyl-5-methyl-1H-pyrazol-1-ylcarbonyl)benzene

The chiral title compound, $[Fe_2(C_5H_5)_2(C_{26}H_{20}N_4O_2)]$, crystallizes as a racemate. The enantiomers are linked by an aromatic π–π stacking interaction into a centrosymmetric dimer.

Comment

The title compound, (I), was synthesized (Shi *et al.*, 2005) as part of an ongoing investigation of the chemistry of organometallic pyrazoles and its crystal structure has been determined (Fig. 1).
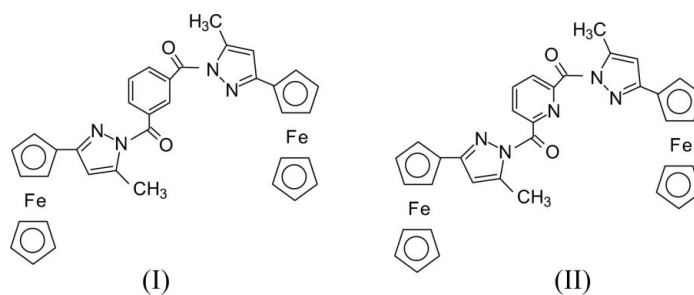
Compound (I) is isomorphous with the previously reported compound, (II) (see scheme) (Shi *et al.*, 2006). Except for the intrinsic differences between the benzene and pyridine rings, the bond distances in (I) and (II) are rather similar (Table 1). Moreover, for each pyrazole ring in the two compounds, the bond distances indicate electron delocalization (Gilchrist, 1997; Shi *et al.*, 2005). However, the most striking difference between (I) and (II) is their molecular conformations. The dihedral angles between the benzene or pyridine ring and the two pyrazole rings [for (I), the N1/C11–C13/N2 and N3/C24–C26/N4 rings; for (II), the N1/C11–C13/N2 and N4/C23–C25/N5 rings] are 74.1 (2) and 63.9 (3)°, respectively, for (I), and 81.7 (2) and 66.1 (2)°, respectively, for (II). For compound (I), the pyrazole ring and the adjacent substituted cyclopentadienyl ring make dihedral angles of 7.3 (3) and 2.9 (3)°, whereas the corresponding values are 6.9 (2) and 1.3 (2)° for compound (II).

Aromatic π–π stacking interactions are found in both compounds. In each compound, the stacking interaction results from the benzene or pyridine ring in the molecule at (x, y, z) and the corresponding ring generated by the symmetry operation $(1 - x, 1 - y, 1 - z)$. The ring-centroid and interplanar separation distances for the rings concerned are 3.794 (3) and 3.461 Å, respectively, for (I), and the corresponding values for (II) are 3.681 (3) and 3.343 Å, respectively, suggesting significant interactions (Glidewell *et al.*, 2005). Thus, aromatic π–π stacking interactions occur between the enantiomers, forming a centrosymmetric dimer.
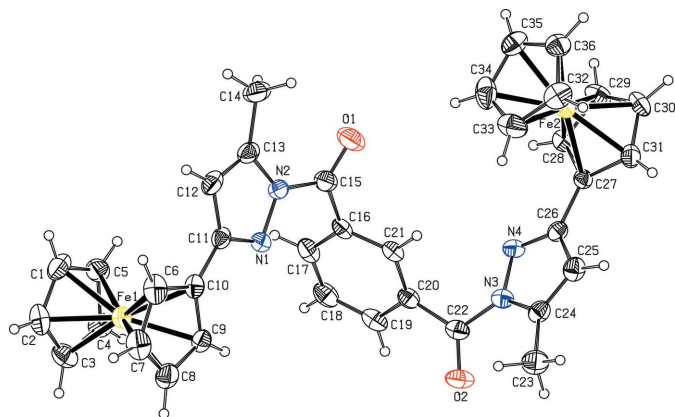
Figure 1
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

A mixture of $SOCl_2$ (4 ml, 55 mmol) and benzene-1,3-dicarboxylic acid (5 mmol) was refluxed under N_2 until the solid disappeared. After removal of $SOCl_2$, the residue was dissolved in tetrahydrofuran (THF; 10 ml) and cooled to 273 K. To this solution were added dropwise Et_3N (2 ml, 14.3 mmol) in THF (5 ml) and 3-ferrocenyl-5-methyl-1H-pyrazole (2.66 g, 10 mmol) in THF (15 ml). The reaction mixture was allowed to reach ambient temperature and was then stirred for 20 h. The solvent was evaporated *in vacuo* and the resulting solid was purifed by chromatography on silica gel with dichloromethane as eluant, to afford an orange–yellow solid (m.p. 460–461 K, yield 54.4%). Orange–red crystals of the title compound suitable for single-crystal X-ray diffraction were obtained from a dichloromethane–acetone mixture (1:1). Spectroscopic analysis: IR (KBr, v, cm^{-1}): 3111 (m, CH), 1691 (vs, O=C), 1587 (m, C=N), 1537 (m, C=C), 1348 (vs, C—N); UV [nm, λ_{max} ($\varepsilon \times 10^4$), in DMF]: 283.00 (2.28) (B-band), 366.00 (0.27) (K-band).

Crystal data

[Fe₂(C₅H₅)₂(C₂₆H₂₀N₄O₂)]
$M_r = 662.34$
Triclinic, $P\bar{1}$
$a = 10.559$ (2) Å
$b = 11.727$ (2) Å
$c = 13.401$ (3) Å
$\alpha = 87.87$ (3)°
$\beta = 67.41$ (3)°
$\gamma = 78.40$ (3)°

$V = 1499.3$ (6) Å^3
$Z = 2$
$D_x = 1.467$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.01$ mm^{-1}
$T = 295$ K
Block, orange–red
$0.20 \times 0.15 \times 0.11$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.824$, $T_{max} = 0.897$
6216 measured reflections

5876 independent reflections
4635 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 26.0°$
3 standard reflections
every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.171$
$S = 1.12$
5876 reflections
399 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 2.3942P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Fe1—C1	2.030 (5)	Fe2—C27	2.024 (4)
Fe1—C2	2.026 (5)	Fe2—C28	2.048 (4)
Fe1—C3	2.035 (5)	Fe2—C29	2.042 (4)
Fe1—C4	2.033 (5)	Fe2—C30	2.045 (4)
Fe1—C5	2.032 (5)	Fe2—C31	2.030 (4)
Fe1—C6	2.030 (5)	Fe2—C32	2.042 (5)
Fe1—C7	2.038 (5)	Fe2—C33	2.034 (5)
Fe1—C8	2.036 (5)	Fe2—C34	2.031 (5)
Fe1—C9	2.037 (4)	Fe2—C35	2.046 (5)
Fe1—C10	2.040 (4)	Fe2—C36	2.039 (5)

All H atoms were placed in geometrically idealized positions and subsequently treated as riding atoms, with C—H distances of 0.93 (aromatic and olefinic) or 0.96 (CH₃) Å and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$.

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

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Gilchrist, T. L. (1997). *Heterocyclic Chemistry*, 3rd ed., pp. 295–297. London: Addison Wesley Longman Ltd.
Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* C**61**, o209–o210.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
McArdle, P. (2005). *OSCAIL-X* for Windows. Version 1.0.4. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
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.
Shi, Y.-C., Zhu, B.-B. & Sui, C.-X. (2006). *Acta Cryst.* E**62**, m1651–m1653.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.