

1-Acetyl-3-ferrocenyl-5-methyl-1*H*-pyrazole and 1-acetyl-5-ferrocenyl-3-(2-pyridyl)-1*H*-pyrazole

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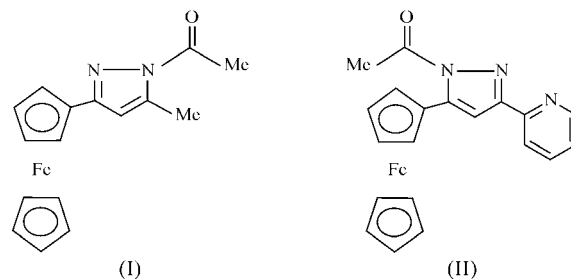
Molecules of 1-acetyl-3-ferrocenyl-5-methyl-1*H*-pyrazole, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{11}\text{H}_{11}\text{N}_2\text{O})]$, form a centrosymmetric dimer generated by a combination of one $\text{C}—\text{H} \cdots \pi$ (pyrazole) and one $\text{C}—\text{H} \cdots \pi$ (cyclopentadienyl) interaction. The dimers are linked by $\text{C}—\text{H} \cdots \pi$ interactions, involving the pyrazole rings as acceptors, into layers parallel to $(10\bar{1})$. Molecules of 1-acetyl-5-ferrocenyl-3-(2-pyridyl)-1*H*-pyrazole, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{15}\text{H}_{12}\text{N}_3\text{O})]$, are linked by $\text{C}—\text{H} \cdots \text{O}$ interactions into a chain running in the $[010]$ direction. Two chains of this type passing through each unit cell are connected by $\text{O} \cdots \pi$ (pyridyl) interactions into an $[010]$ double chain.

Comment

Recently, pyrazole-based compounds have attracted much attention because their set of donor atoms, N_3 and N_2E ($\text{E} = \text{O}$ and S), are used as important ligands to model the active sites of metalloenzymes and to recognize metal ions (Gross & Vahrenkamp, 2005; Scarpellini *et al.*, 2005; Miranda *et al.*, 2005). Some of their complexes can be used as catalysts and potential drugs (Ajellal *et al.*, 2006; Porchia *et al.*, 2005).

Acylation of tautomeric 3(5)-ferrocenyl-5(3)-methyl-1*H*-pyrazole with acetyl chloride afforded the first of the title compounds, (I) (Shi *et al.*, 2006), while 5(3)-ferrocenyl-3(5)-(2-pyridyl)-1*H*-pyrazole, synthesized by our group after acylation of the pyrazolyl NH group, generated the second of the title compounds, (II). Since 3-(2-pyridyl)-1*H*-pyrazole acts as a multifunctional ligand having several coordination modes (Hu *et al.*, 2006) and exhibiting plentiful coordination chemistry from dinuclearity to multinuclearity (Lam *et al.*, 1997), compound (II) is expected to afford an interesting coordination chemistry *via* the set of N_2O donor atoms, *viz.* one pyridine N atom, one pyrazole N atom and one carbonyl O atom, whereas (I) can act as an *N,O*-bidentate organometallic ligand on coordination to a metal ion. In view of the redox activity and non-linear optical property of the ferrocenyl group, compounds (I) and (II) are also expected to have potential uses as new materials. For a fully unequivocal characteriza-

tion, the crystal structures of the title compounds have been determined (Figs. 1 and 2).



As in *N,N'*-butanedioylbis(5-ferrocenyl-3-methyl-1*H*-pyrazole), the bond lengths of each pyrazole ring in (I) and (II) indicate electron delocalization (Shi *et al.*, 2005; Tables 1 and 3). The dihedral angles between the pyrazole ring and, respectively, the corresponding substituted cyclopentadienyl ring and the corresponding acetyl plane are 21.52 (11) and 2.9 (3)° for (I), and 28.7 (2) and 9.7 (4)° for (II). Furthermore, for (II), the pyrazole and pyridine rings make a dihedral angle of 4.47 (18)°. As expected, the small dihedral angle of 0.65 (13)° for (I) and 1.4 (2)° for (II) between the unsubstituted cyclopentadienyl ring and the substituted cyclopentadienyl ring indicates that the two cyclopentadienyl rings are parallel to each other. The $\text{C}3 \cdots \text{Cg}2 \cdots \text{Cg}3 \cdots \text{C}10$ torsion angle of 6.43 (15)° for (I) and 5.6 (3)° for (II), where $\text{Cg}2$ and $\text{Cg}3$ are the centroids of rings $\text{C}1—\text{C}5$ and $\text{C}6—\text{C}10$, respectively, indicates that the two cyclopentadienyl rings of the ferrocenyl group in each of (I) and (II) are nearly in an eclipsed conformation, as was previously observed in a ferrocene-containing compound (Erasmus *et al.*, 1996).

Interestingly, the above dihedral angles and the $\text{C}10—\text{C}11$ bond length for (I) and the $\text{C}10—\text{C}11$ and $\text{C}13—\text{C}14$ bond lengths for (II) (which are shorter than the value of 1.48 Å for a $\text{Csp}^2—\text{Csp}^2$ single bond) suggest that the pyrazole rings of (I) and (II) are each slightly conjugated with the corresponding substituted cyclopentadienyl ring and the pyridine ring (Tables 1 and 3).

Although compounds (I) and (II) both crystallize in the space group $P2_1/n$, their packing modes are different. Since the pyrazole ring electrons are delocalized, an intermolecular three-centre $\text{C}—\text{H} \cdots (\text{N})_2$ hydrogen bond indicates that there

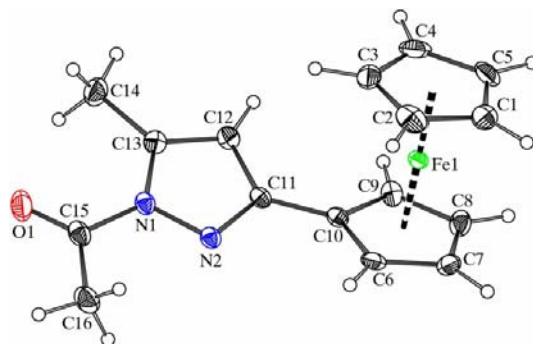


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

exists a C—H··· π interaction involving the pyrazole ring in the crystalline state of (I) (Glidewell *et al.*, 2005; Sylvestre *et al.*, 2005; Table 2). Atoms C2 and C16 in the molecule at (x , y , z) act as hydrogen-bond donors, *via* atoms H2 and H16B, to the pyrazole ring (N1/N2/C11–C13) and the unsubstituted C1–C5 cyclopentadienyl ring in the molecule at ($1 - x$, $1 - y$, $1 - z$), so leading to the formation of a centrosymmetric dimer (Fig. 3). The dimer is linked into a [010] double chain with the

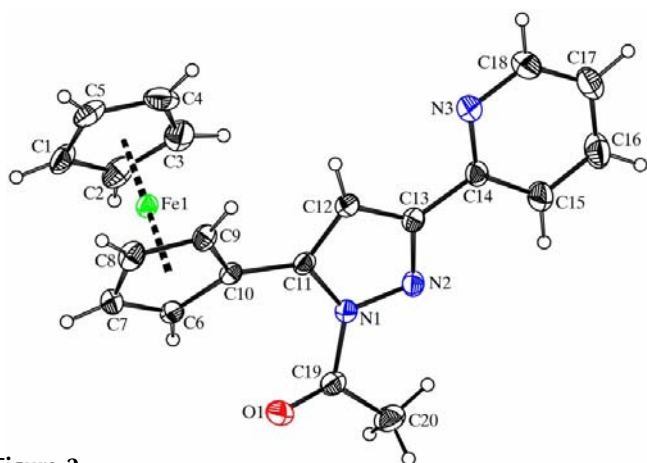


Figure 2

The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

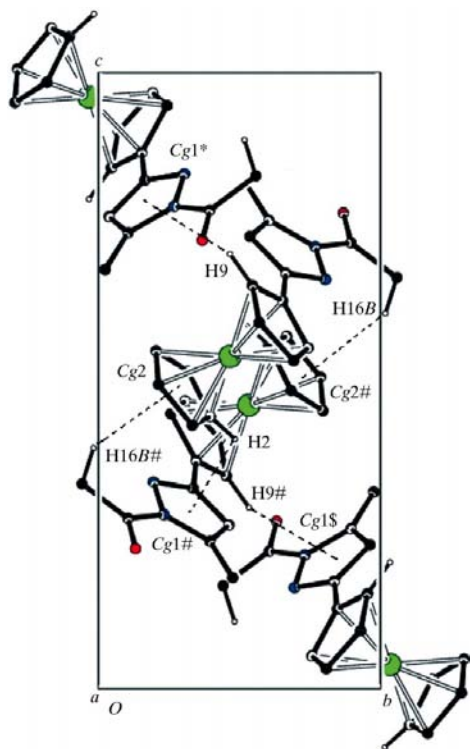


Figure 3

Part of the crystal structure of (I), showing the formation of a [010] chain. Cg1 and Cg2 are the centroids of the N1/N2/C11–C13 and C1–C5 rings, respectively. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions ($\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$), ($1 - x$, $1 - y$, $1 - z$) and ($-\frac{3}{2} + x$, $\frac{1}{2} - y$, $-\frac{3}{2} + z$), respectively. For clarity, H atoms not involved in the motifs shown have been omitted.

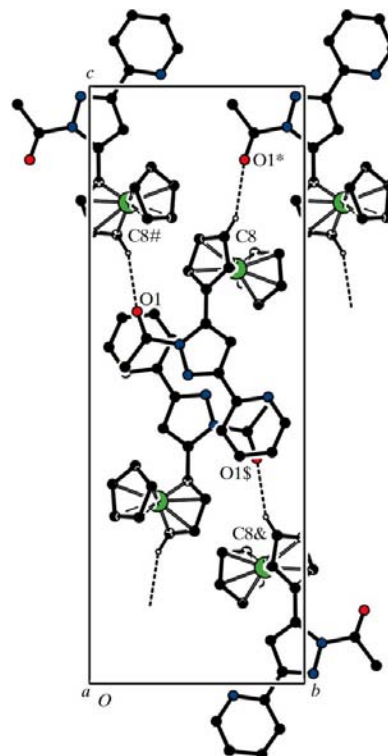


Figure 4

Part of the crystal structure of (II), showing the formation of a [010] chain. Atoms marked with an asterisk (*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions ($\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), ($\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$), ($1 - x$, $1 - y$, $1 - z$) and ($-\frac{3}{2} + x$, $\frac{1}{2} - y$, $-\frac{3}{2} + z$), respectively. For clarity, H atoms not involved in the motifs shown have been omitted.

2_1 screw axis along ($\frac{3}{4}$, y , $\frac{3}{4}$) by hydrogen bonds in which atom C9 in the substituted cyclopentadienyl ring of the molecule at (x , y , z) acts as a hydrogen-bond donor, *via* atom H9, to the pyrazole ring in the molecule at ($\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$), and the pyrazole ring in the molecule at (x , y , z) acts as a hydrogen-bond acceptor and atom C9 in the molecule at ($\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$) as a hydrogen-bond donor.

In contrast, intermolecular C—H···O interactions are present in the crystalline state of (II) and the N atoms do not participate in hydrogen-bond formation (Table 4). Atom C8 in the substituted cyclopentadienyl ring of the molecule at (x , y , z) acts as a hydrogen-bond donor, *via* atom H8, to atom O1 in the molecule at ($\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), and atom O1 in the molecule at (x , y , z) acts in turn as a hydrogen-bond acceptor and atom C8 in the molecule at ($\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$) as a hydrogen-bond donor (Fig. 4). Molecules of (II) form a [010] chain and generate a 2_1 screw axis along ($\frac{3}{4}$, y , $\frac{3}{4}$) *via* these intermolecular C—H···O hydrogen bonds. Two chains of this type through each unit cell are linked by O··· π contacts (Jara *et al.*, 2006; Spek, 2003) into a [010] double chain [O1···Cg4ⁱ = 3.913 (3) Å, C19···Cg4ⁱ = 3.864 (3) Å and C19—O1···Cg4ⁱ = 78.9 (2)°; symmetry code: (i) $1 - x$, $1 - y$, $1 - z$; Cg4 is the centroid of the N3/C14–C18 ring].

Experimental

To a solution of 3(5)-ferrocenyl-5(3)-methyl-1*H*-pyrazole (1.33 g, 5 mmol) and Et₃N (1.423 g, 14 mmol) in tetrahydrofuran (10 ml) was

added dropwise acetyl chloride (1 ml, 14 mmol) in tetrahydrofuran (5 ml) at ambient temperature. The reaction mixture was stirred for 1 h. After removal of the solvent, the resulting solid was washed with water, air-dried, and recrystallized from dichloromethane and petroleum ether to afford the orange title compound (I) (yield 62.2%; m.p. 440.15–441.15 K). Analysis calculated for $C_{16}H_{16}FeN_2O$: C 62.36, H 5.23, N 9.09%; found: C 62.15, H 5.28, N 9.32%. IR (KBr, cm^{-1}): 1721 (ν_s , O=C). UV (λ_{max} , in DMF, nm): 256.00 (2.68×10^4 , B band), 328.00 (0.05×10^4 , R band). 1H NMR ($CDCl_3$): δ 6.200 (1H, s, CH), 4.694, 4.332 (s, 2H, s, 2H, C_5H_4), 4.102 (s, 5H, C_5H_5), 2.704 (s, 3H, $COCH_3$), 2.603 (s, 3H, CH_3). The corresponding reaction of 5(3)-ferrocenyl-3(5)-(2-pyridyl)-1H-pyrazole (1.646 g, 5 mmol), acetyl chloride (2 ml, 28 mmol) and Et_3N (3.036 g, 30 mmol), *via* chromatography on silica gel with dichloromethane as eluant, gave the orange-red title compound (II) (yield 47.2%; m.p. 423.65–424.45 K). Analysis calculated for $C_{20}H_{17}FeN_3O$: C 64.71, H 4.62, N 11.32%; found: C 64.71, H 4.57, N 11.46%. IR (KBr, cm^{-1}): 1724 (ν_s , CO). UV (λ_{max} , in DMF, nm): 278.00 (2.32×10^4 , B band), 374.00 (0.1×10^4 , K band), 451.00 (0.046×10^4 , *d-d* band). 1H NMR (600 MHz, $CDCl_3$): δ 8.703–8.699, 8.123–8.110, 7.810–7.784, 7.329–7.309 (*d*, 1H, *d*, 1H, *t*, 1H, *q*, 1H, C_5H_4N), 7.200 (*s*, 1H, CH), 4.745, 4.364 (*s*, 2H, *s*, 2H, C_5H_4), 4.170 (*s*, 5H, C_5H_5), 2.809 (*s*, 3H, CH_3).

Compound (I)

Crystal data

$[Fe(C_5H_5)(C_{11}H_{11}N_2O)]$	$Z = 4$
$M_r = 308.16$	$D_x = 1.477 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 11.8781 (18) \text{ \AA}$	$\mu = 1.08 \text{ mm}^{-1}$
$b = 7.2993 (10) \text{ \AA}$	$T = 193 \text{ K}$
$c = 16.088 (2) \text{ \AA}$	Block, orange
$\beta = 96.353 (5)^\circ$	$0.50 \times 0.35 \times 0.16 \text{ mm}$
$V = 1386.3 (3) \text{ \AA}^3$	

Data collection

Rigaku Mercury diffractometer	14815 measured reflections
ω scans	3178 independent reflections
Absorption correction: multi-scan (Jacobson, 1998)	2964 reflections with $I > 2\sigma(I)$
$T_{min} = 0.613$, $T_{max} = 0.846$	$R_{int} = 0.024$
	$\theta_{max} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.841P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.11$	$\Delta\rho_{max} = 0.44 \text{ e \AA}^{-3}$
3178 reflections	$\Delta\rho_{min} = -0.38 \text{ e \AA}^{-3}$
184 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

O1—C15	1.211 (2)	C10—C11	1.455 (2)
N1—N2	1.383 (2)	C11—C12	1.420 (3)
N1—C13	1.387 (2)	C12—C13	1.362 (3)
N1—C15	1.406 (2)	C13—C14	1.492 (3)
C11—N2	1.321 (2)	C15—C16	1.489 (3)
N2—C11—C10	121.01 (16)	O1—C15—N1	119.84 (19)
N2—C11—C12	111.56 (16)	O1—C15—C16	124.36 (19)
C10—C11—C12	127.41 (16)	N1—C15—C16	115.80 (18)
N2—N1—C13	111.77 (14)	C11—C12—C13	106.50 (16)
N2—N1—C15	119.51 (16)	N1—C13—C14	125.05 (17)
C13—N1—C15	128.68 (16)	C12—C13—N1	105.62 (16)
C11—N2—N1	104.55 (14)	C12—C13—C14	129.30 (19)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$Cg1$ and $Cg2$ are the centroids of the N1/N2/C11–C13 and C1–C5 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots Cg1 ⁱ	1.00	2.85	3.408 (2)	116
C9—H9 \cdots Cg1 ⁱⁱ	1.00	2.64	3.567 (2)	154
C16—H16B \cdots Cg2 ⁱ	0.98	2.96	3.704 (3)	133
C9—H9 \cdots N1 ⁱⁱ	1.00	2.56	3.380 (3)	139
C9—H9 \cdots N2 ⁱⁱ	1.00	2.48	3.457 (3)	166

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Compound (II)

Crystal data

$[Fe(C_5H_5)(C_{15}H_{12}N_3O)]$	$Z = 4$
$M_r = 371.22$	$D_x = 1.486 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.4790 (15) \text{ \AA}$	$\mu = 0.92 \text{ mm}^{-1}$
$b = 8.9290 (18) \text{ \AA}$	$T = 295 \text{ K}$
$c = 24.942 (3) \text{ \AA}$	Plate, orange-red
$\beta = 94.84 (3)^\circ$	$0.21 \times 0.13 \times 0.11 \text{ mm}$
$V = 1659.7 (5) \text{ \AA}^3$	

Data collection

Enraf–Nonius CAD-4 diffractometer	3247 independent reflections
$\omega/2\theta$ scans	2548 reflections with $I > 2\sigma(I)$
Absorption correction: empirical <i>via</i> ψ scan (North <i>et al.</i> , 1968)	$R_{int} = 0.023$
$T_{min} = 0.830$, $T_{max} = 0.901$	$\theta_{max} = 26.0^\circ$
3503 measured reflections	3 standard reflections
	every 200 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 1.3303P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.10$	$\Delta\rho_{max} = 0.44 \text{ e \AA}^{-3}$
3247 reflections	$\Delta\rho_{min} = -0.47 \text{ e \AA}^{-3}$
226 parameters	
H-atom parameters constrained	

Table 3

Selected bond lengths (\AA) for (II).

O1—C19	1.193 (4)	C10—C11	1.465 (4)
N1—N2	1.378 (3)	C11—C12	1.358 (4)
N1—C11	1.396 (4)	C12—C13	1.406 (4)
N1—C19	1.422 (4)	C13—C14	1.471 (4)
N2—C13	1.319 (4)	C19—C20	1.489 (5)

Table 4

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8—H8 \cdots O1 ⁱ	0.93	2.54	3.416 (4)	158

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

All H atoms were located in difference maps and were treated as riding atoms, with C—H distances of 0.95 (pyrazolyl), 0.98 (methyl) and 1.00 \AA (cyclopentadienyl) at 193 K for (I), and C—H distances of 0.93 (CH) and 0.96 \AA (CH_3) at 295 K for (II), and with $U_{iso}(H)$ values of $1.2U_{eq}(C)$ or $1.5U_{eq}(methyl\ C)$. The H atoms of the C20 methyl group in (II) were modelled as six equally spaced half H atoms.

For (I), data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2001). For (II), data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3053). Services for accessing these data are described at the back of the journal.

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