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[1-(2-Hydroxyethyl)-5-methylpyrazol-3-yl]-ferrocenium chloride and [1-(2-hydroxyethyl)-5-methylpyrazol-3-yl]ferrocene cocrystal

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The title compound, $[Fe(C_5H_5)(C_{11}H_{13}N_2O)]\cdot[Fe(C_5H_5)(C_{11}H_{13}N_2O)]Cl$, cocrystallizes as (1–2-hydroxyethyl-5-methylpyrazol-3-yl)ferrocenium chloride–(1-2-hydroxyethyl-5-methylpyrazol-3-yl)ferrocene (1/1). Two independent pyrazolylferrocenes in the asymmetric unit, with similar geometric parameters, form an $R_4^4(24)$ tetramer *via* O—H···N hydrogen bonds and Cl^- ions occupy the spaces between the tetramer rings. This tetramer is linked *via* C—H···π hydrogen bonds, involving the cyclopentadienyl rings as acceptors, into a [100] chain.

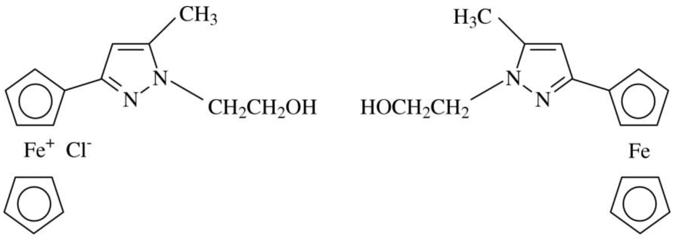
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.010 Å
Disorder in solvent or counterion
R factor = 0.068
wR factor = 0.189
Data-to-parameter ratio = 14.1

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

Comment

Pyrazole-based compounds are important because some of them are used as ligands to model the active sites of metalloenzymes and for the recognition of metal ions (Gross & Vahrenkamp, 2005; Scarpellini *et al.*, 2005; Miranda *et al.*, 2005). Some of their complexes can also be used as catalysts and potential drugs (Ajellal *et al.*, 2006; Porchia *et al.*, 2005). As part of an ongoing investigation of the chemistry of ferrocenylpyrazoles (Shi *et al.*, 2005; Shi *et al.*, 2006*a*,*b*), the title compound, (I) (Fig. 1), has been synthesized by the reaction of 2-hydroxyethylhydrazine and ferrocenoylacetone.



(I)

The asymmetric unit of (I) consists of an oxidized ferrocene, [1-(2-hydroxyethyl)-5-methylpyrazol-3-yl]ferrocenium chloride, (I*a*), and a neutral [1-(2-hydroxyethyl)-5-methylpyrazol-3-yl]ferrocene molecule, (I*b*). Bond lengths and angles in the ferrocenes are in normal ranges (Cambridge Structural Database, Version 5.27, with August 2006 update; Allen, 2002). Both ferrocenyl units adopt eclipsed conformations [C1—*Cg*2—*Cg*3—C10 = 0.4 (5)° and C17—*Cg*5—*Cg*6—C22 = −1.4 (5)°, where *Cg*2, *Cg*3, *Cg*5 and *Cg*6 are the centroids of the rings C1–C5, C6–C10, C17–C21 and C22–C26, respectively]. The dihedral angle between the cyclopentadienyl rings in the oxidized ferrocene [3.4 (4)°] is slightly larger than in the neutral molecule [0.5 (4)°]. Moreover, the dihedral angle between the pyrazole ring and the adjacent cyclopentadienyl ring is 9.3 (4)° for (I*a*) and 3.7 (3)° for (I*b*).

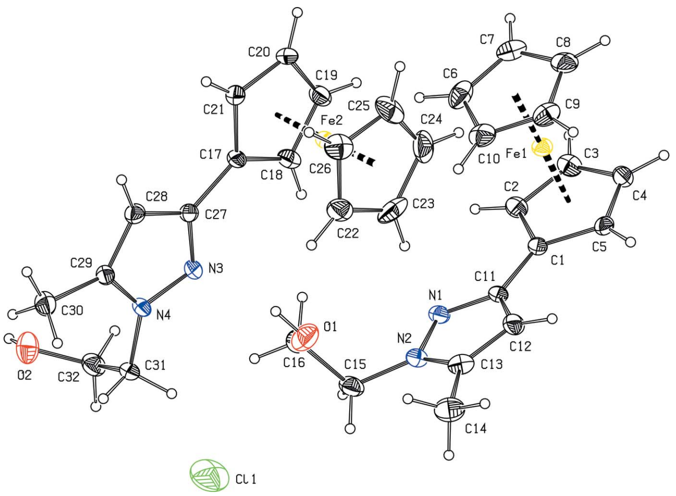


Figure 1
The asymmetric unit of (I). The major Cl disorder component is shown. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

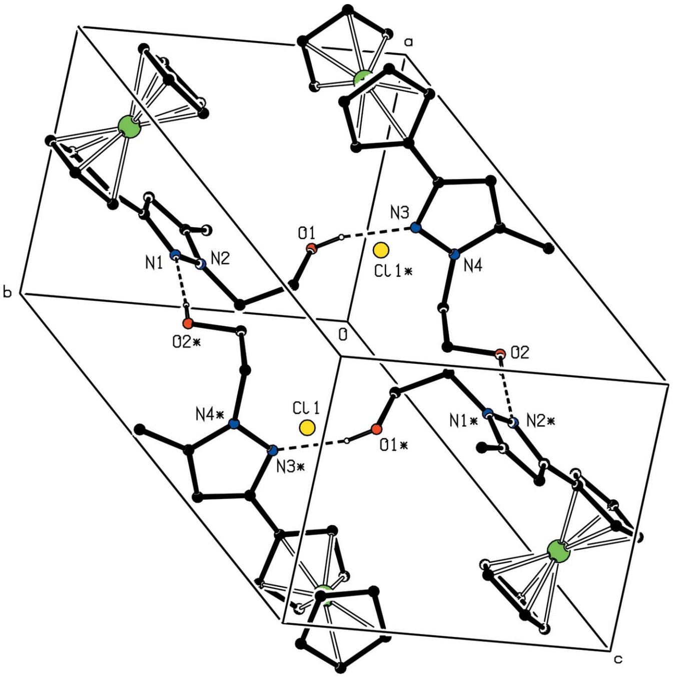


Figure 2
The unit-cell contents, illustrating the tetranuclear entity linked together by hydrogen bonds (dashed lines) into a ring. The rings are stacked above each other and the Cl^- ions occupy the spaces between the rings. The major Cl disorder component is shown. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

In the crystal structure of (I), each of the two independent pyrazolylferrocenes in the asymmetric unit has a C—H···O intramolecular hydrogen bond and acts as both a donor and an acceptor of intermolecular hydrogen bonds, so generating an $R_4^4(24)$ tetramer (Fig. 2) via O—H···N hydrogen bonds. The Cl^- ions occupy the spaces between the tetramer rings. In addition, the tetramer is linked by C—H···π interactions involving the cyclopentadienyl rings (C6–C10)^{ii} as acceptors, into a [100] chain (symmetry code as in Table 1).

Experimental

An ethanol (20 ml) solution of 2-hydroxyethylhydrazine (0.38 g, 5 mmol) and ferrocenoylacetone (1.35 g, 5 mmol) in the presence of *p*-TsOH (ca 10 mg) was refluxed overnight. The solvent was evaporated *in vacuo* and the resulting oil was purified by chromatography on silica gel with diethyl ether and dichloromethane (2:1 *v*/*v*) as eluant, to afford the first orange–yellow band, (1-(2-hydroxyethyl)-3-methylpyrazol-5-yl)ferrocene (m.p. 354.05–354.75 K; yield 24%) and the second orange–yellow band (m.p. 366.85–367.65 K; yield 30%). Orange crystals of the title compound, (I), suitable for single-crystal X-ray diffraction were obtained from a solution of the second band in dichloromethane–petroleum ether (1:1 *v*/*v*). Microelemental analysis, calculated for $C_{32}H_{36}ClFe_2N_4O_2$: C 58.61, H 5.53, N 8.54%; found: C 59.13, H 5.62, N 8.63%. ^1H NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 7.259 (1H, *s*, HO), 5.970 (1H, *s*, CH), 4.833, 4.455 (2H, 2H, 2*s*, C_5H_4), 4.219 (5H, *s*, C_5H_5), 4.107 (2H, *t*, OCH_2), 3.988 (2H, *t*, NCH_2), 2.259 (3H, *s*, CH_3).

Crystal data

$[Fe(C_5H_5)(C_{11}H_{13}N_2O)]\cdot[Fe(C_5H_5)(C_{11}H_{13}N_2O)]Cl$
$M_r = 655.80$
Triclinic, $P\overline{1}$
$a = 9.161$ (2) Å
$b = 11.307$ (1) Å
$c = 16.318$ (1) Å
$\alpha = 80.05$ (2)°
$\beta = 79.84$ (2)°
$\gamma = 68.49$ (2)°
$V = 1537.1$ (4) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.07$ mm^{-1}
$T = 295$ K
0.21 × 0.17 × 0.14 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.801$, $T_{max} = 0.861$
5795 measured reflections
5421 independent reflections
3712 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
3 standard reflections
frequency: 120 min
intensity decay: 0.1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.189$
$S = 1.05$
5421 reflections
384 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*3 is the centroid of the C6–C10 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···N3	0.85	1.96	2.794 (6)	166
O2—H2O···N1^{i}	0.85	2.02	2.861 (6)	172
C14—H14*A*···O1	0.96	2.54	3.276 (10)	133
C14—H14*C*···*Cg*3^{ii}	0.96	2.96	3.777 (9)	144
C30—H30*A*···O2	0.96	2.72	3.420 (8)	131

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, y, z$.

Aryl and alkyl H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å, and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2$–1.5 times $U_{eq}(C)$. The methyl groups were rotated to fit the electron density. Hydroxyl H atoms were positioned geometrically and refined as riding, with O—H = 0.85 Å and $U_{iso}(H) = 1.2U_{eq}(O)$. The Cl atom is disordered over two sites; the site occupancy factors refined to 0.681 (12) and 0.319 (12).

m1386 Shi *et al.* • $[Fe(C_5H_5)(C_{11}H_{13}N_2O)]\cdot[Fe(C_5H_5)(C_{11}H_{13}N_2O)]Cl$ *Acta Cryst.* (2007). E**63**, m1385–m1387

Data collection: *CAD-4 VAX/PC Fortran System* (Enraf–Nonius, 1988); cell refinement: *CAD-4 VAX/PC Fortran System*; data reduction: *XCAD4* (Harms & Wocadlo, 1997) in *WinGX* (Farrugia, 1999); 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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Acta Cryst. (2007). E**63**, m1385–m1387 Shi *et al.* • $[Fe(C_5H_5)(C_{11}H_{13}N_2O)]\cdot[Fe(C_5H_5)(C_{11}H_{13}N_2O)]Cl$ **m1387**