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N,*N*′-Bis(2-pyridylmethyl)ferrocene-1,1′-diyldicarboxamide and *N*,*N*′-bis(3-pyridylmethyl)ferrocene-1,1′-diyldicarboxamide

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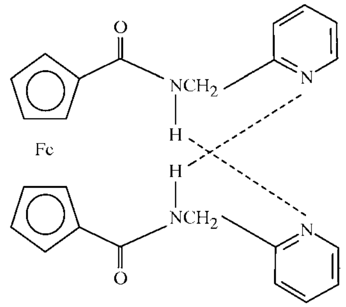
The molecules of *N*,*N*′-bis(2-pyridylmethyl)ferrocene-1,1′-diyldicarboxamide, $[Fe(C_{12}H_{11}N_2O)_2]$, contain intramolecular N—H···N hydrogen bonds and are linked into sheets by three independent C—H···O hydrogen bonds. The molecules of the isomeric compound *N*,*N*′-bis(3-pyridylmethyl)ferrocene-1,1′-diyldicarboxamide lie across inversion centres, and the molecules are linked into sheets by a combination of N—H···N hydrogen bonds and π–π stacking interactions between pyridyl groups.

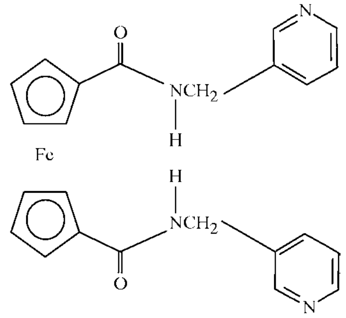
Comment

Amide groups, because of their unique stereoelectronic character, can interact with electron-deficient centres through carbonyl groups and with electron-rich centres through N—H units. This dual character has been used successfully for the design of amide-based receptors for recognizing a variety of guests, including cations, anions and neutral molecules (Ranganathan *et al.*, 1998; Kumar *et al.*, 2003). Ferrocenyl compounds possess redox-responsive character and they can be used for electrochemical recognition of guests (Bernhardt & Creevey, 2004). In view of the above essential components for the molecular and electrochemical recognition of anionic guests, we have designed and synthesized the title compounds, (I) and (II) (Figs. 1 and 2), and report their structures here.

The most striking difference between (I) and (II) lies in their conformations. In (I), the two substituents attached to the cyclopentadienyl groups are synclinal, whereas in (II), they are antiperiplanar, as indicated by the torsion angles C5···*Cg*1···*Cg*2···C17 [69.3 (2)°; *Cg*1 and *Cg*2 are the centroids of the C1–C5 and C13–C17 rings, respectively] for (I) and C5···*Cg*1···*Cg*1*···C5* [−180.0 (2)°; *Cg*1 and *Cg*1* are the centroids of the C1–C5 and C1*–C5* rings, respectively] for (II). Moreover, the dihedral angles between the cyclopentadienyl groups and the amide planes (O1/C6/N1 and O2/C18/N3) are 4.3 (3) and 8.7 (3)° in (I); the corresponding values for (II) are 16.5 (3) and 16.5 (3)°. However, the bond dimensions in (I) and the centrosymmetric compound (II) are similar, except that the N1—C7 and N3—C19 bond lengths in (I) are shorter than the N1—C7 and N1* —C7* bond lengths in (II), and the N1—C7—C8 and N3—C19—C20 bond angles in (I) are larger than those in (II) (Tables 1 and 3). For each of (I) and (II), the bonds linking the cyclopentadienyl groups and the carbonyl groups are typical of a single bond (Csp^2—Csp^2); this fact suggests that the carbonyl group is not involved in conjugation with the cyclopentadienyl group (Shi *et al.*, 2006).



(I)



(II)

Although both compounds crystallize in the same space group, they show markedly different packing modes (Figs. 3

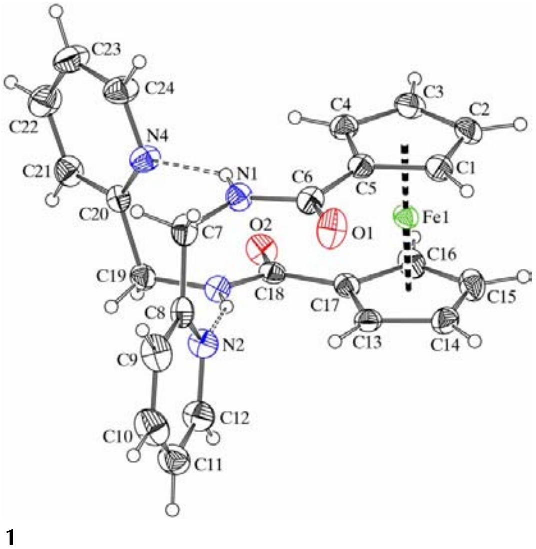


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are drawn as dashed lines.

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and 4). Compound (I) displays intermolecular C—H···O═C hydrogen bonds in addition to intramolecular N—H···N hydrogen bonds (Table 2). Atom C11 of the 2-pyridyl group in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H11, to carbonyl atom O2 in the molecule at (x, $1 + y$, z), so generating a chain in the [010] direction. Two chains of this type passing through each unit cell are linked by C—H···O═C hydrogen bonds in which atom C12 of the 2-pyridyl group in the molecule at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O2 in the molecule at ($1 - x$, $1 - y$, $1 - z$), thus leading to an [010] double chain along with the formation of an $R_2^2(24)$ (Bernstein *et al.*, 1995) ring (Fig. 3). Two such double chains are further linked along the [001] direction *via* a C—H···O═C hydrogen bond involving atom C1 of the cyclopentadienyl group and carbonyl atom O1 in the molecule at ($1 - x$, $1 - y$, $-z$), thus resulting in a chain parallel to [001] along with the formation of an $R_2^2(10)$ ring. The combination of the [001] chain and the [010] double chain leads to a two-dimensional network.

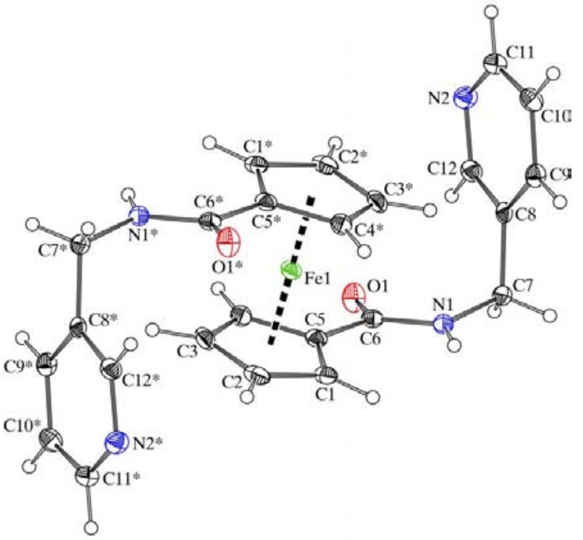

Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Symmetry equivalents related by ($1 - x$, $1 - y$, $1 - z$) are also shown and indicated by asterisks. Displacement ellipsoids are drawn at the 30% probability level.

Unlike those of (I), the molecules of compound (II) lie across inversion centres and are linked by intermolecular N—H···N hydrogen bonds (Table 4). Atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H1N, to pyridyl atom N2 in the molecule at ($1 + x$, y, z) to form a [100] chain. The chain passing through each unit cell is further linked along [010] by a π–π stacking interaction between the 3-pyridyl group in the molecule at (x, y, z) and the corresponding group in the molecule at ($-x$, $2 - y$, $-z$) to give an [010] chain; the ring-centroid separation and interplanar distance are 3.668 (2) and 3.361 Å, respectively (Glidewell *et al.*, 2005). The combination of the [100] and [010] chains generates a two-dimensional network.

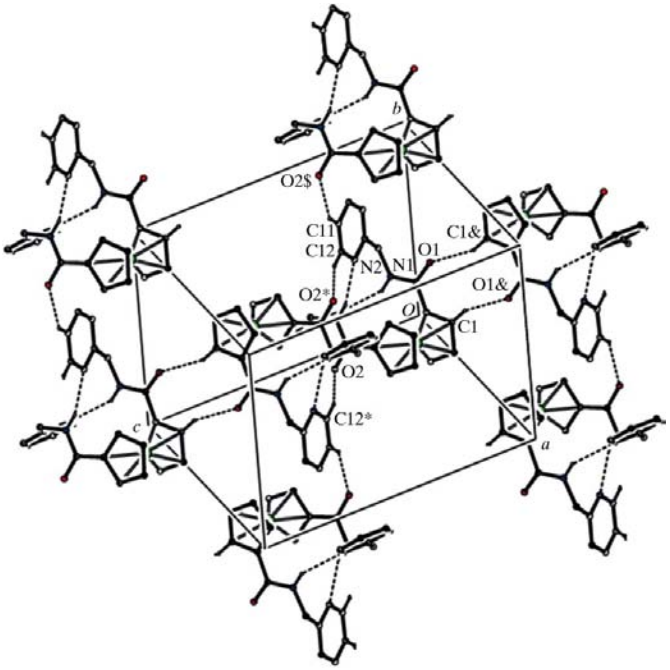

Figure 3
The crystal structure of (I). Hydrogen bonds are drawn as dashed lines. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), dollar sign ($) or ampersand (&) are at the symmetry positions ($1 - x$, $1 - y$, $1 - z$), (x, $1 + y$, z) and ($1 - x$, $1 - y$, $-z$), respectively.

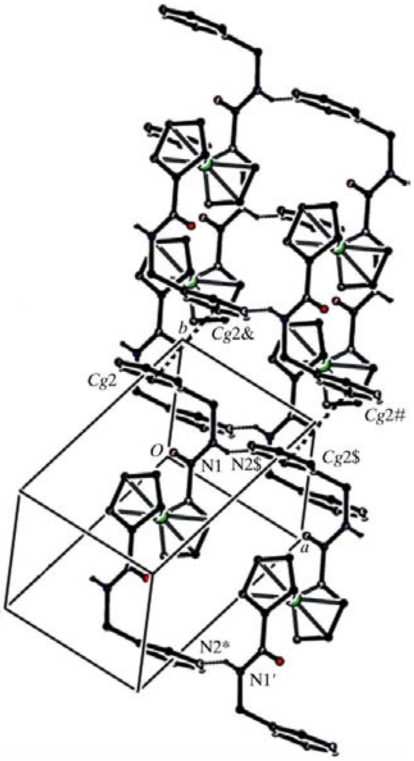

Figure 4
The crystal structure of (II). Hydrogen bonds are drawn as dashed lines. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), dollar sign ($) or prime (′) are at the symmetry positions ($1 - x$, $1 - y$, $1 - z$), ($1 + x$, y, z) and ($2 - x$, $1 - y$, $1 - z$), respectively; *Cg*2 is centroid of the pyridyl ring; *Cg*2$, *Cg*2& and *Cg*2# are at the symmetry positions ($1 + x$, y, z), ($-x$, $2 - y$, $-z$) and ($1 - x$, $2 - y$, $-z$), respectively.

Experimental

A mixture of oxalyl chloride (3 ml, 34.4 mmol), ferrocene-1,1′-dicarboxylic acid (1.37 g, 5 mmol) and DMF (0.5 ml) in dichloromethane (20 ml) was stirred under nitrogen to give a clear solution. After removal of excess oxalyl chloride, the residue was dissolved in tetrahydrofuran (THF, 10 ml); to the solution was added dropwise a mixture of NEt_3 (3.036 g, 30 mmol) and 2-pyridylmethylamine or 3-pyridylmethylamine (0.757 g, 7 mmol) in THF (25 ml). The mixture was stirred overnight. The resulting crude solid was collected, washed with water, air-dried and recrystallized from 95% ethanol to afford the orange title compounds [(I): m.p. 499.55–500.25 K, yield 57%; (II): m.p. 474.95–475.05 K, yield 51%]. For (I), analysis calculated for $C_{24}H_{22}FeN_4O_2$: C 63.45, H 4.88, N 12.33%; found: C 63.50, H 4.72, N 12.51%. IR (KBr): 3273 (*m*, NH), 1648 (*vs*, O═C) cm^{-1}. UV [λ_{max}, ($\varepsilon \times 10^4$), in DMF]: 263.00 (2.78, B-band), 345.00 (0.17, R-band), 431.00 (0.09, d-d band) nm. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.032 (2H, *s*, 2NH), 8.602, 7.764, 7.469, 7.292 (2H, *s*, 2H, *s*, 2H, *s*, 2H, *s*, $2C_5H_4N$), 4.748, 4.350 (4H, *s*, 4H, *s*, $2C_5H_4$), 4.551 (4H, *s*, $2CH_2$). For (II), analysis calculated for $C_{24}H_{22}FeN_4O_2$: C 63.45, H 4.88, N 12.33%; found: C 63.49, H 4.76, N 12.31%. IR (KBr): 3217 (*m*, NH), 1642 (*vs*, O═C) cm^{-1}. UV [λ_{max}, ($\varepsilon \times 10^4$), in DMF]: 264.00 (2.93, B-band), 310.50 (1.02, R-band), 503.50 (0.13, d-d band) nm. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.578 (2H, *s*, 2NH), 8.495–8.514, 8.467–8.474, 7.750–7.763, 7.372–7.393 (2H, *t*, 2H, *d*, 2H, *d*, 2H, *q*, $2C_5H_4N$), 4.759, 4.231 (4H, *s*, 4H, *s*, $2C_5H_4$), 4.403–4.413 (4H, *d*, $2CH_2$).

Compound (I)

Crystal data

$[Fe(C_{12}H_{11}N_2O)_2]$
$M_r = 454.31$
Triclinic, $P\bar{1}$
$a = 8.9859$ (2) Å
$b = 9.8987$ (2) Å
$c = 13.7459$ (3) Å
$\alpha = 100.297$ (2)°
$\beta = 102.114$ (2)°
$\gamma = 114.051$ (1)°
$V = 1042.75$ (4) Å^3
$Z = 2$
$D_x = 1.447$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.75$ mm^{-1}
$T = 295$ K
Prism, orange
0.23 × 0.15 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)
$T_{min} = 0.858$, $T_{max} = 0.914$
14739 measured reflections
4769 independent reflections
3611 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 27.5°$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.105$
$S = 1.07$
4769 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.4231P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C5—C6	1.480 (4)	C17—C18	1.477 (3)
C6—O1	1.231 (3)	C18—O2	1.233 (3)
C6—N1	1.346 (3)	C18—N3	1.337 (3)
C7—N1	1.444 (3)	C19—N3	1.442 (3)
N1—C7—C8	114.6 (2)	N3—C19—C20	114.03 (19)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···N4	0.86	2.30	3.079 (3)	151
N3—H3N···N2	0.86	2.16	2.974 (3)	157
C1—H1···O1^{i}	0.98	2.52	3.452 (4)	159
C11—H11···O2^{ii}	0.93	2.43	3.173 (4)	137
C12—H12···O2^{iii}	0.93	2.49	3.374 (4)	158

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

Compound (II)

Crystal data

$[Fe(C_{12}H_{11}N_2O)_2]$
$M_r = 454.31$
Triclinic, $P\bar{1}$
$a = 6.386$ (3) Å
$b = 7.882$ (3) Å
$c = 9.987$ (4) Å
$\alpha = 85.305$ (17)°
$\beta = 89.53$ (2)°
$\gamma = 84.831$ (19)°
$V = 499.0$ (4) Å^3
$Z = 1$
$D_x = 1.512$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.79$ mm^{-1}
$T = 193$ K
Block, orange
0.30 × 0.25 × 0.10 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.811$, $T_{max} = 0.917$
4908 measured reflections
1810 independent reflections
1602 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 25.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.082$
$S = 1.09$
1810 reflections
143 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 0.3145P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C6	1.235 (3)	N1—C7	1.454 (3)
N1—C6	1.349 (3)	C5—C6	1.483 (3)
N1—C7—C8	110.49 (19)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···N2^{i}	0.88	2.15	2.952 (3)	151

Symmetry code: (i) $x + 1, y, z$.

All H atoms in (I) and (II) were placed at geometrically idealized positions and subsequently treated as riding atoms, with C—H distances of 0.93 (pyridyl group), 0.97 (CH_2) or 0.98 Å (cyclopentadienyl group) and N—H distances of 0.86 Å for (I), and C—H distances of 0.95 (pyridyl group), 0.99 (CH_2) or 1.00 Å (cyclopentadienyl group) and N—H distance of 0.88 Å for (II); U_{iso}(H) values were set at $1.2U_{eq}$(C,N).

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989) for (I) and *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001) for (II); cell refinement: *CAD-4 Software* for (I) and *CrystalClear* for (II); data reduction: *XCAD4* (Harms & Wocadlo, 1995) for (I) and *CrystalStructure* (Rigaku/MSC, 2004) for (II); program(s) used to solve structure: *OSCAILX* (McArdle, 2005) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAILX* and *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: GD3052). Services for accessing these data are described at the back of the journal.

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