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Intermolecular (pyrrole)N—H···π(pyrrole) interactions in bis(2-pyrrolyl)methylferrocene, an organometallic porphyrin precursor

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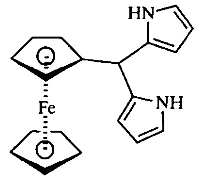
Abstract

The title compound, $C_{19}H_{18}FeN_2$ or $[Fe(C_5H_5)(C_{14}H_{13}N_2)]$, crystallizes in space group $P2_1/n$ with two molecules in the asymmetric unit. The pyrrole groups take part in intermolecular (pyrrole)N—H···π(pyrrole) interactions through a hydrogen-bonded ring system involving four pyrrole groups, with N···(pyrrole centroid) distances in the range 3.209 (3)–3.427 (3) Å and N—H···(pyrrole centroid) angles in the range 127–139°.

Comment

Dipyrromethane derivatives are useful building blocks in the synthesis of porphyrin model systems, with direct approaches to *trans*-substituted porphyrins available by condensation of dipyrromethanes with aldehydes (Lee & Lindsey, 1994). In contrast to porphyrin chemistry, there has been a paucity of structural reports on dipyrromethanes and their hydrogen-bonding interactions (Lin *et al.*, 1996; Bennis & Gallagher, 1998). The influence of weak hydrogen bonds in crystal packing has been commented on (Gallagher, Ferguson, Böhmer & Kraft, 1994; Ferguson *et al.*, 1996; Braga *et al.*, 1998), although a fundamental understanding of the control and exploitation of X—H···π interactions (X = C, N, O) remains an undeveloped field in crystal engineering (Steiner, 1997). This contrasts with the systematic study and exploitation of strong donors and acceptors in molecular-recognition systems (Etter *et al.*, 1990). In molecules where several different potential hydrogen-bond donors and acceptors are present (with cooperativity and/or competition among these interactions), the ability to deduce in advance the molecular-packing arrangements largely remains an unrealized vision (Wolff, 1996) and is principally due to the unpredictable nature of weaker hydrogen bonds in stabilizing three-dimensional structures.

Recent reports on N—H···π interactions include aliphatic N—H donors with conventional aromatic acceptors, *e.g.* phenyl rings (Allen *et al.*, 1997; Starikov & Steiner, 1998). Atypical heteroaromatic N—H donor and acceptor systems have also been described, where indole groups (Krishna *et al.*, 1999), pyrrole groups (Lin *et al.*, 1996; Goddard *et al.*, 1997; Bennis & Gallagher, 1998) and pyrazole ligands (Beringhelli *et al.*, 1998) take part in (heteroaromatic)N—H···π(heteroaromatic) interactions. These unusual examples of hydrogen bonds are important in facilitating our understanding of important molecular-recognition processes in biological systems, as well as in advancing crystal engineering studies. We report herein the structure of bis(2-pyrrolyl)methylferrocene, (I), where intermolecular N—H···π(pyrrole) interactions arise in a system with pyrrole N—H donors and pyrrole groups as acceptors.



(I)

Compound (I) crystallizes in space group $P2_1/n$ with two independent molecules, A and B, in the asymmetric unit (Fig. 1). Bond lengths and angles are in accord with anticipated values (Orpen *et al.*, 1994). The molecules differ in conformation, and torsion-angle differences are evident from the C11—C1—C41—N45 values of −170.0 (3) (A) and 175.5 (3)° (B) (Table 1). The weighted r.m.s. fit for the superposition of the non-disordered non-H atoms of molecules A and B (inverted) is 0.35 Å (Spek, 1998). The unsubstituted cyclopentadienyl ring of molecule B is disordered over two sites with occupancies of 0.68 (2) and 0.32 (2). Rotational disorder is often observed in the unsubstituted C_5 ring of ferrocene derivatives, *e.g.* 1-ferrocenyl-1-phenylethanol (Ferguson *et al.*, 1993). The dihedral angle between the C_5 planes are 1.1 (3) (A) and 3.6 (9)° (B), with the rings staggered by 15.7 (3) and 33.6 (7)° from an eclipsed

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conformation in *A* and *B* (major isomer), respectively. The relevant values for the minor component are 4 (2) and 1.5 (16)°, respectively. The Csp^3 atoms C1*A*/*B* are displaced by 0.045 (5) and 0.114 (5) Å from the substituted C$_5$ ring plane away from the Fe atom. The two independent pyrrole groups, C31*n*–N35*n* and C41*n*–N45*n* (where *n* = *A* or *B*), are oriented at angles of 84.15 (10) and 87.35 (10)° to one another in *A* and *B*, respectively; these are similar to the angle of 86.43 (9)° in 1,4-bis(di-2-pyrrolylmethyl)benzene, (II) (Bennis & Gallagher, 1998), but larger than the angle of 64.28 (18)° in *meso*-(3,5-di-tertbutylphenyl)dipyrromethane, (III) (Lin *et al.*, 1996). Examination of (I) with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

In the asymmetric unit, molecules *A* and *B* associate in pairs with each of the four pyrrole groups taking part in intermolecular (pyrrole)N—H···π(pyrrole) interactions in a hydrogen-bonded ring system. A weak Csp^3—H···π(pyrrole) interaction links the pyrrole moieties into a one-dimensional chain (Fig. 2 and Table 2). This hydrogen-bonding arrangement contrasts with the two-dimensional network of (pyrrole)N—H···π(pyrrole) hydrogen bonds in (II) and the one-dimensional relay of (pyrrole)N—H···π(pyrrole) and (pyrrole)N—H···π(phenyl) interactions in (III). Intermolecular (pyrrole)N—H···π(pyrrole) interactions generate a one-dimensional chain in pyrrole (Goddard *et al.*, 1997).

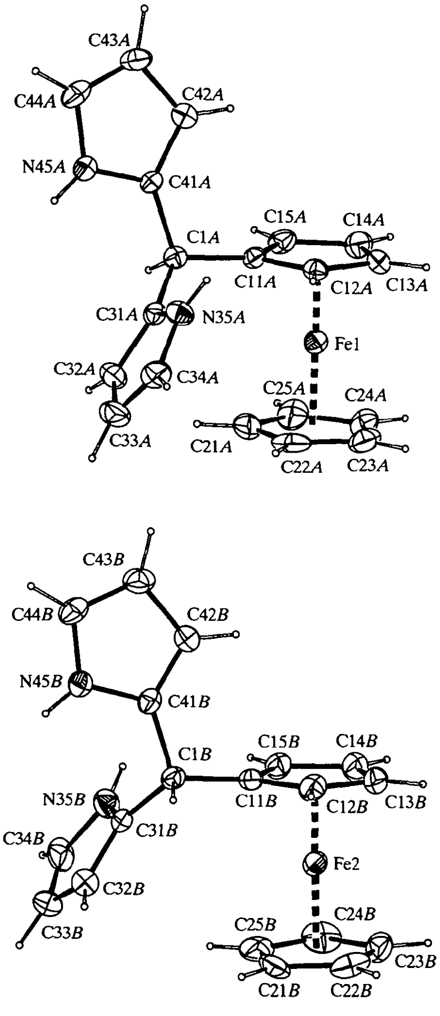

Fig. 1. Views of molecules *A* and *B* with the atomic numbering scheme. The major conformation of the C21*B* ring is depicted. Displacement ellipsoids are drawn at the 30% probability level.

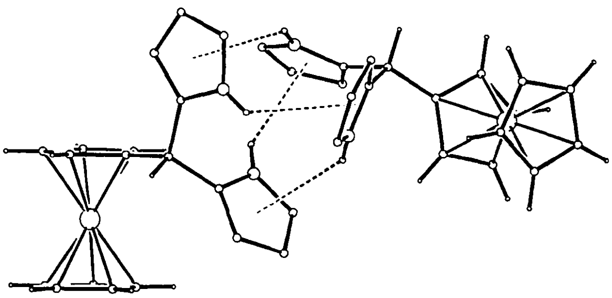

Fig. 2. A view of the (pyrrole)N—H···π(pyrrole) intermolecular interactions in the crystal structure of (I).

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for molecules containing the pyrrolyl (C_4H_3NH) group shows that the majority of such structures display conventional N—H···{O, N, S, *X* (= halide)}-type hydrogen bonding when such acceptors are available. In the structures of (I), (II) and (III), weak (pyrrole)N—H···π(pyrrole) interactions dominate in the absence of stronger hydrogen-bond donors and acceptors. The hydrogen-bonding patterns in the crystal structures of a diverse range of ferrocene alcohol derivatives (Ferguson *et al.*, 1993; Gallagher, Ferguson, Glidewell & Zakaria, 1994) have also been reported. Further studies are in progress on N—H···π(pyrrole) interactions in related porphyrin precursors.

Experimental

The title compound was prepared by a similar method to that reported for 1,4-bis(di-2-pyrrolylmethyl)benzene (Lee & Lindsey, 1994). Ferrocenecarboxaldehyde (1.49 g) was dissolved in pyrrole (15 ml) and stirred for 30 min. Three drops of trifluoroacetic acid were added and the solution stirred for 20 h. Addition of CH_2Cl_2 (100 ml) and washing with two 30 ml aliquots of 0.1 mol dm^{-3} NaOH gave an orange–brown solution. Pyrrole and dichloromethane were removed under reduced pressure and the resulting brown solid was washed with cyclohexane. Yellow crystals were grown from CH_2Cl_2 solution [yield 1.8 g, 78%; m.p. 383–385 K (uncorrected)]. IR ν_{max} (KBr, cm^{-1}): 3352, 1666, 1555, 1467, 1409, 1279, 1259; UV-Vis ($CHCl_3$, nm): 384, 343, 232; ^{1}H NMR (400 MHz, δ, $CHCl_3$, p.p.m.): 2.17 [1H, *s*, (pyrrolyl)$_2$CH], 4.09 (5H, *s*,

C_5H_5), 4.07 (2H, *m*, C_5H_4), 4.15 (2H, *m*, C_5H_4), 6.00, 6.14, 6.64 (3 × 2H, *br m*, pyrrolyl C—H), 7.92 (2H, *br s*, N—H).

Crystal data

$[Fe(C_5H_5)(C_{14}H_{13}N_2)]$
$M_r = 330.20$
Monoclinic
$P2_1/n$
$a = 15.5486\ (10)$ Å
$b = 7.7295\ (5)$ Å
$c = 25.647\ (3)$ Å
$\beta = 96.005\ (6)°$
$V = 3065.4\ (4)$ Å^3
$Z = 8$
$D_x = 1.431$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10.19$–$15.48°$
$\mu = 0.981$ mm^{-1}
$T = 290\ (1)$ K
Needle
0.26 × 0.16 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: Gaussian (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.842$, $T_{max} = 0.878$
5892 measured reflections
5684 independent reflections

3227 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.4°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 9$
$l = -31 \rightarrow 31$
3 standard reflections
frequency: 120 min
intensity variation: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.076$
$S = 0.932$
5684 reflections
428 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.275$ e Å^{-3}
$\Delta\rho_{min} = -0.293$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0006 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C31*A*—N35*A*	1.371 (4)	C31*B*—N35*B*	1.365 (4)
C31*A*—C32*A*	1.369 (4)	C31*B*—C32*B*	1.359 (4)
C32*A*—C33*A*	1.422 (4)	C32*B*—C33*B*	1.407 (5)
C33*A*—C34*A*	1.355 (5)	C33*B*—C34*B*	1.342 (5)
C34*A*—N35*A*	1.367 (4)	C34*B*—N35*B*	1.371 (4)
C41*A*—N45*A*	1.358 (3)	C41*B*—N45*B*	1.365 (4)
C41*A*—C42*A*	1.363 (4)	C41*B*—C42*B*	1.354 (4)
C42*A*—C43*A*	1.417 (4)	C42*B*—C43*B*	1.421 (4)
C43*A*—C44*A*	1.344 (4)	C43*B*—C44*B*	1.360 (4)
C44*A*—N45*A*	1.369 (4)	C44*B*—N45*B*	1.363 (4)
Fe1—C11*A*—C1*A*	128.3 (2)	Fe2—C11*B*—C1*B*	131.0 (2)
C11*A*—C1*A*—C31*A*	114.4 (2)	C11*B*—C1*B*—C31*B*	114.1 (3)
C11*A*—C1*A*—C41*A*	110.0 (2)	C11*B*—C1*B*—C41*B*	109.2 (2)
C31*A*—C1*A*—C41*A*	113.0 (2)	C31*B*—C1*B*—C41*B*	113.4 (2)

C31*A*—C1*A*—C11*A*—Fe1	55.5 (3)
C41*A*—C1*A*—C11*A*—Fe1	−176.1 (2)
C11*A*—C1*A*—C31*A*—N35*A*	64.9 (4)
C11*A*—C1*A*—C41*A*—N45*A*	−170.0 (3)
C31*B*—C1*B*—C11*B*—Fe2	−45.5 (4)
C41*B*—C1*B*—C11*B*—Fe2	−173.6 (2)
C11*B*—C1*B*—C31*B*—N35*B*	−64.7 (4)
C11*B*—C1*B*—C41*B*—N45*B*	175.5 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 represent the centroids of the pyrrole rings C31*A*–N35*A*, C41*A*–N45*A*, C31*B*–N35*B* and C41*B*–N45*B*, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N35*A*—H35*A*···*Cg*4	0.86	2.51	3.209 (3)	139
N45*A*—H45*A*···*Cg*3	0.86	2.73	3.339 (3)	129
N35*B*—H35*B*···*Cg*1	0.86	2.74	3.427 (3)	138
N45*B*—H45*B*···*Cg*2	0.86	2.81	3.391 (3)	127
C1*A*—H1*A*···*Cg*2^{i}	0.98	2.84	3.807 (3)	168

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

Molecule (I) crystallized in the monoclinic system (space group $P2_1/n$ from the systematic absences). H atoms were treated as riding atoms (N—H 0.86 and C—H 0.93–0.98 Å). It was evident during the penultimate stage of refinement {when $R[F^2 > 2\sigma(F^2)]$ was 0.06} that there were minor components of disorder associated with the unsubstituted cyclopentadienyl ring bonded to Fe2. Coordinates for the minor component were generated and the *AFIX*59 instruction was subsequently used for both major and minor components together with appropriate *DELU* and *ISOR* controls. Refinement of the non-H atoms with anisotropic displacement parameters gave final site-occupancy factors of 0.68 (2) and 0.32 (2), in agreement with a Fourier cross-section through the disordered ring using *PLATON* (Spek, 1998).

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP8* (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1024). Services for accessing these data are described at the back of the journal.

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exo-[(*RS*,*SR*)-*N*,*N'*-Bis(salicylidene)-2,3-butanediaminato]oxovanadium(IV)

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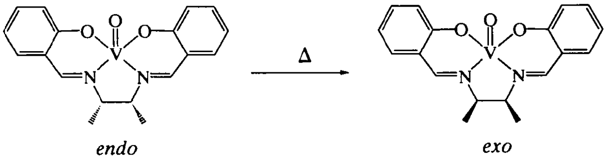
Abstract

The thermally more stable isomer of the title complex, {2,2′-[(*RS*,*SR*)-2,3-butanediylbis(nitrilomethylidene)]diphenolato-*O*,*N*,*N′*,*O′*}oxovanadium(IV), $[VO(C_{18}H_{18}N_2O_2)]$ or [VO(sal-*meso*-bn)] [H_2sal-*meso*-bn is (*RS*,*SR*)-*N*,*N′*-bis(salicylidene)-2,3-butanediamine], in the solid state, has been determined to be the *exo* isomer. The two methyl groups of the central diamine moiety in the Schiff base ligand are on the same side of the N_2O_{oxo} plane of the VN_2O_3 square pyramid as the oxo ligand. The V=O distance is 1.595 (2) Å, and the V atom is displaced by 0.50 (1) Å toward the oxo ligand from the N_2O_2 basal plane. There is an intermolecular $V\cdots O_{salicyl}$ close contact of 2.972 (2) Å, which is *trans* to the V=O bond.

Comment

Certain oxovanadium(IV) complexes with Schiff base ligands show thermal isomerization and/or dehydrogenation of the Schiff base ligand in the solid state (Kojima *et al.*, 1994; Hoshina *et al.*, 1998). The title complex shows thermal isomerization at 483 K. For this complex, there are two possible geometrical isomers, *endo* and *exo*, arising from the disposition of the substituents of the alkyldiamine moiety of the Schiff base ligand relative to the VN_2O_3 square pyramid. In this paper, the structure of the more stable *exo* isomer, (I), is reported.



(I)

As shown in Fig. 1, the two methyl groups at C14 and C16 are located on the same side as the oxo ligand, O2. This is the *exo* isomer. The present study reveals that thermal isomerization of the title complex occurs in the solid state from the *endo* to the *exo* isomer. The central five-membered chelate ring adopts a symmetric skew conformation. The methyl groups on C14 and C16 are in axial and equatorial positions, respectively, to the five-membered chelate ring.

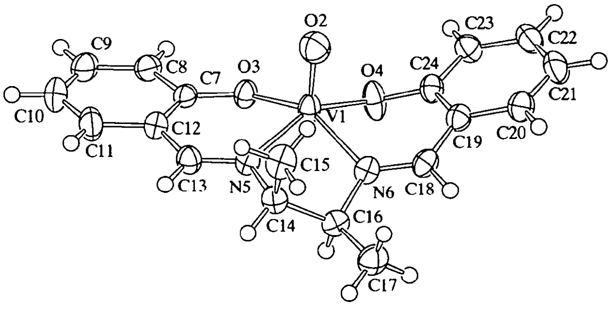


Fig. 1. The molecular structure of (I) showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The crystal structure of (I) is shown in Fig. 2. The complexes form a weak dimeric structure around the centre of symmetry through cyclic $V1\cdots O4^i—V1^i\cdots O4$ interactions, with a $V1\cdots O4^i$ distance of 2.972 (2) Å [symmetry code: (i) $1-x$, $-y$, $2-z$]. This interaction causes the deformation of the six-membered chelate