Table 6. *Selected geometric parameters (Å, °) for (III)*

(Co,Mn)—Cl(1)	2.259 (3)	(Co,Mn)—N(1)	1.974 (9)
(Co,Mn)—N(4)	1.969 (11)	(Co,Mn)—Cl(1^{i})	2.259 (3)
(Co,Mn)—N(1^{i})	1.974 (9)	(Co,Mn)—N(4^{i})	1.969 (11)
N(1)—C(2)	1.491 (18)	N(1)—C(7)	1.479 (17)
N(4)—C(5)	1.483 (17)	N(4)—C(3^{i})	1.485 (19)
C(2)—C(3)	1.553 (20)	C(3)—N(4^{i})	1.485 (19)
C(6)—C(7)	1.500 (21)	C(6)—C(5)	1.465 (19)
Cl(1)—(Co,Mn)—N(1)	91.3 (3)	C(5)—N(4)—C(3^{i})	111.3 (10)
N(1)—(Co,Mn)—N(4)	92.0 (5)	C(2)—C(3)—N(4^{i})	107.0 (11)
N(1)—(Co,Mn)—Cl(1^{i})	88.7 (3)	N(1)—C(7)—C(6)	111.0 (11)
Cl(1)—(Co,Mn)—N(1^{i})	88.7 (3)	Cl(1)—(Co,Mn)—N(4)	91.5 (3)
N(4)—(Co,Mn)—N(1^{i})	88.0 (5)	Cl(1)—(Co,Mn)—Cl(1^{i})	180.0 (1)
Cl(1)—(Co,Mn)—N(4^{i})	88.5 (3)	N(4)—(Co,Mn)—Cl(1^{i})	88.5 (3)
N(4)—(Co,Mn)—N(4^{i})	180.0 (1)	N(1)—(Co,Mn)—N(1^{i})	180.0 (1)
N(1^{i})—(Co,Mn)—N(4^{i})	92.0 (5)	Cl(1^{i})—(Co,Mn)—N(1^{i})	91.3 (3)
(Co,Mn^{i})—N(1)—C(2^{i})	106.8 (7)	N(1)—(Co,Mn)—N(4^{i})	88.0 (5)
(Co,Mn)—N(1)—C(7)	119.4 (8)	Cl(1^{i})—(Co,Mn)—N(4^{i})	91.5 (3)
C(2)—N(1)—C(7)	110.7 (10)	N(1^{i})—C(2)—C(3^{i})	107.9 (10)
(Co,Mn)—N(4)—C(5)	121.4 (9)	C(7)—C(6)—C(5)	115.1 (12)
(Co,Mn)—N(4)—C(3^{i})	108.3 (8)	N(4)—C(5)—C(6)	110.9 (11)

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

All three structures were solved by direct methods using *SOLV* in *SHELXTL-Plus* (Sheldrick, 1991). Lattice water molecules were identified in each structure. The refinement of (I) was straightforward, with the metal site assumed to be solely occupied by Cu^{II}. The metal-site occupancies in (II) and (III) were set equal to the ratio of metal ions found by chemical analyses. For (III), one water-molecule site had excess electron density. It was assumed that the Co^{II} ion had been oxidized to Co^{III} and the following site occupancies were assigned: (Co,Mn) Co 0.5, Mn 0.5; (Cl,O) Cl 0.5, O 0.5. During the final stages of refinement, the displacement parameters of the two metal atoms were constrained have identical values. For the Cl and O atoms occupying the (Cl,O) site, both the positional and displacement parameters were so constrained.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1206). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyanoferrocene: a Two-Dimensional Network Generated by Short C—H···N Hydrogen Bonds

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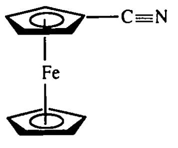
Abstract

In cyanoferrocene, [Fe(C$_5$H$_5$)(C$_6$H$_4$N)], the N atom acts as a hydrogen-bond acceptor from C—H bonds in two other molecules. Each molecule is thus hydrogen-bonded to four others, forming sheets.

Comment

Simple cyanobenzenes often exhibit intermolecular C—H···N—C hydrogen bonds in the solid state and examples include benzonitrile (C$_6$H$_5$CN), where the intermolecular C···N distance across the hydrogen bond is 3.51 (1) Å (Fauvet, Massaux & Chevalier, 1978), 1,4-dicyanobenzene, where the corresponding distance is also 3.51 (1) Å (Guth, Heger & Drück, 1982), 1,3,5-tricyanobenzene in its 1:1 molecular complex with hexamethylbenzene, where the tricyanobenzene forms discrete layers interleaved with layers of hexamethylbenzene and in which there are four intermolecular C···N distances of 3.471 (4) and two of 3.516 (6) Å (Reddy, Goud, Panneerselvam & Desiraju, 1993), and 1,2,4,5-tetracyanobenzene, in which each of the four independent N atoms forms several close intermolecular C···N contacts (Prout & Tickle, 1973), although the precision of this determination, from visually estimated photographic data, is not high. The cyclopentadienyl rings in ferrocene are more electron rich than benzene rings, thus allowing the possibility of a higher negative charge on the N atom of a cyano substituent on the C$_5$ ring, as compared with the N atom of a cyanobenzene moiety. This in turn opens up the possibility of stronger intramolecular C—H···N—C hydrogen bonds in the ferrocene series. We report here the structure of cyanoferrocene, $[(C_5H_5)Fe(C_5H_4CN)]$, (I), which does indeed exhibit short C—H···N—C hydrogen bonds.



(I)

The ferrocene fragment has a conformation close to eclipsed, as is usual in monosubstituted ferrocenes, with a mean C1*n*—*Cg*1—*Cg*2—C2*n* (*n* = 1–5; *Cg*1 and *Cg*2 are the centroids of rings C11–C15 and C21–C25, respectively) twist angle of 8.0 (7)°; the angle subtended at the Fe atom by the ring centroids is 179.2 (2)°. The internal C—C—C angle at the C atom bearing the cyano substituent does not show the enhancement typically found in cyanobenzenes (Prout & Tickle, 1973; Guth, Heger & Drück, 1982). The C—C bond lengths in the substituted cyclopentadienyl ring are significantly longer than those in the unsubstituted ring; the exocyclic bond lengths are typical of their types (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The principal interest, however, lies in the intermolecular interactions (Fig. 1).

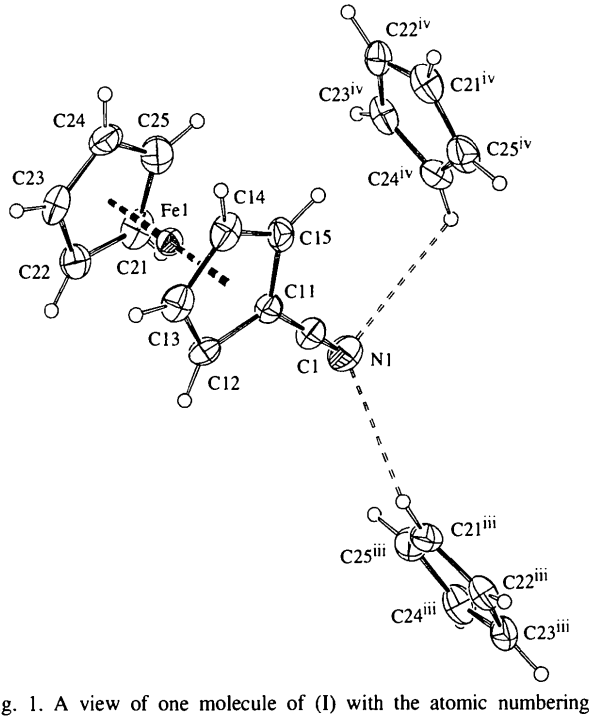
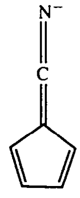
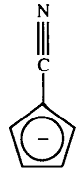


Fig. 1. A view of one molecule of (I) with the atomic numbering scheme and 30% probability displacement ellipsoids, showing also the C—H···N hydrogen bonds to adjacent cyclopentadiene rings [symmetry codes: (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, 2-z$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$].

Atom N1 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond acceptor from atom C21 in the molecule at $(-\frac{1}{2}+x, \frac{1}{2}-y, 2-z)$, *i.e.* (iii), and from atom C24 in the molecule at $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$, *i.e.* (iv), with C···N distances of 3.384 (6) and 3.381 (6) Å, respectively, which are significantly shorter than those observed in cyanobenzenes (Fauvet, Massaux & Chevalier, 1978; Guth, Heger & Drück, 1982; Reddy, Goud, Panneerselvam & Desiraju, 1993); the corresponding N···H distances (based on riding H atoms, with C—H 0.93 Å) are 2.70 and 3.00 Å, respectively (Table 3). The second of these probably represents a rather weak interaction despite the similar C···N distance. Repetition of these interactions gives rise to spirals around the screw axes parallel to the **a** and **b** directions. Equivalently, atoms C21 and C24 in the molecule at (*x*, *y*, *z*) act as donors to the N1 atoms in molecules at $(\frac{1}{2}+x, \frac{1}{2}-y, 2-z)$, *i.e.* (i), and $(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, *i.e.* (ii), respectively. Each molecule thus acts as a hydrogen-bond donor to two others and as a hydrogen-bond acceptor from two others, giving rise to sheets perpendicular to the **c** direction. The N1 atom exhibits trigonal coordination, comprising the bond to C1 and the two hydrogen bonds (Fig. 1); the angles C1—N1···H21^{iii} and C1—N1···H24^{iv} are 110 and 109°, respectively, while the H21^{iii}···N1···H24^{iv} angle is 120°. An electronic structure calculation for the isolated cyanocyclopentadienide ligand, $(C_5H_4CN)^-$, made using the *AM*1 method (Dewar, Zoebisch, Healy & Stewart, 1985), shows evidence of a significant contribution from form *A*, having two lone pairs at nitrogen, as well as from form *B*, having only one. This behaviour, if reproduced in cyanoferrocene itself, is consistent with the observed hydrogen bonding.



A



B

While the cyclopentadienyl rings in ferrocene derivatives have been observed in a number of examples to act as acceptors in hydrogen bonds of type O—H···π-C_5H_5 (Glidewell, Klar, Lightfoot, Zakaria & Ferguson, 1996), the behaviour of such rings as hydrogen-bond donors is unusual.

Experimental

Cyanoferrocene was prepared from ferrocenecarboxaldehyde *via* ferrocenecarboxaldoxime (Broadhead, Osgerby & Pauson, 1958). Crystals suitable for single-crystal diffraction were grown from cyclohexane solution.

Crystal data

$[Fe(C_5H_5)(C_6H_4N)]$	Mo $K\alpha$ radiation
M_r = 211.04	λ = 0.7107 Å

Orthorhombic
$P2_12_12_1$
$a = 7.6314 (6)$ Å
$b = 10.4521 (15)$ Å
$c = 11.2292 (14)$ Å
$V = 895.7 (2)$ Å^3
$Z = 4$
$D_x = 1.565$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 11.56–20.02°$
$\mu = 1.626$ mm^{-1}
$T = 294 (1)$ K
Plate
0.42 × 0.42 × 0.22 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans at 4° steps (North, Phillips & Mathews, 1968)
$T_{\min} = 0.497$, $T_{\max} = 0.690$
1504 measured reflections

1504 independent reflections
1155 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max} = 29.86°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0375$
$wR(F^2) = 0.1039$
$S = 0.934$
1504 reflections
119 parameters
H atoms riding (*SHELXL*93 defaults; C—H 0.93 Å)
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.325$ e Å^{-3}
$\Delta\rho_{\min} = -0.289$ e Å^{-3}

Extinction correction: *SHELXL*93
Extinction coefficient: 0.012 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.03 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Fe1	0.23818 (6)	0.11232 (5)	0.70318 (5)	0.0352 (2)
N1	0.2133 (5)	0.3543 (4)	0.9854 (4)	0.0653 (12)
C1	0.1758 (6)	0.3141 (4)	0.8952 (4)	0.0475 (10)
C11	0.1260 (5)	0.2658 (4)	0.7809 (4)	0.0426 (9)
C12	−0.0046 (6)	0.1681 (5)	0.7579 (5)	0.0470 (10)
C13	−0.0054 (6)	0.1455 (5)	0.6328 (4)	0.0553 (12)
C14	0.1212 (7)	0.2294 (5)	0.5799 (4)	0.0548 (12)
C15	0.2028 (6)	0.3027 (4)	0.6698 (4)	0.0477 (11)
C21	0.4076 (7)	0.0332 (5)	0.8230 (4)	0.0553 (12)
C22	0.2888 (6)	−0.0581 (4)	0.7842 (4)	0.0533 (11)
C23	0.3097 (7)	−0.0695 (5)	0.6611 (5)	0.0563 (13)
C24	0.4371 (7)	0.0148 (5)	0.6238 (5)	0.0595 (13)
C25	0.4980 (7)	0.0794 (5)	0.7253 (6)	0.066 (2)
*Cg*1†	0.0880 (6)	0.2223 (5)	0.6843 (4)	
*Cg*2†	0.3882 (7)	−0.0000 (5)	0.7235 (5)	

† *Cg*1 and *Cg*2 are the centroids of rings C11–C15 and C21–C25, respectively.

Table 2. *Selected geometric parameters (Å, °)*

Fe1—*Cg*1	1.637 (5)	C13—C14	1.435 (7)
Fe1—*Cg*2	1.656 (5)	C14—C15	1.411 (6)
N1—C1	1.133 (6)	C21—C22	1.387 (7)
C1—C11	1.432 (6)	C21—C25	1.384 (8)
C11—C12	1.450 (7)	C22—C23	1.396 (7)
C11—C15	1.431 (6)	C23—C24	1.378 (7)
C12—C13	1.425 (7)	C24—C25	1.404 (8)
*Cg*1—Fe1—*Cg*2	179.2 (2)	N1—C1—C11	178.8 (5)
C11—*Cg*1—*Cg*2—C21	8.5 (6)	C14—*Cg*1—*Cg*2—C24	7.2 (6)
C12—*Cg*1—*Cg*2—C22	7.2 (6)	C15—*Cg*1—*Cg*2—C25	8.7 (6)
C13—*Cg*1—*Cg*2—C23	8.5 (6)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
C21—H21···N1$^{\rm i}$	0.93	2.70	3.384 (6)	131
C24—H24···N1$^{\rm ii}$	0.93	3.00	3.381 (6)	106

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

Examination of the structure with *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC Software*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON*, *PLUTON* (Spek 1995*b*). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* (macro *PREPCIF*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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