Ferrocenecarboxylic acid–1,4-diazabicyclo[2.2.2]octane (2/1): sheets built from O—H···N and C—H···O hydrogen bonds

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In the title compound, $2[Fe(C_5H_5)(C_6H_5O_2)]\cdot C_6H_{12}N_2$, the molecular components are linked into finite three-component aggregates by strong O—H···N hydrogen bonds [O···N 2.578 (4) and 2.604 (5) Å; O—H···N 170 (5) and 174 (6)°]; these aggregates are further linked by C—H···O hydrogen bonds [C···O 3.327 (5)–3.401 (5) Å; C—H···O 149–157°] into continuous sheets in the form of (6,3) nets.

Comment

The trigonally trisubstituted acid 3,5-dinitrobenzoic acid forms adducts with a wide range of ditertiary amines having stoichiometry (acid)₂·(base) (Burchell, Glidewell *et al.*, 2001). In each of these adducts, where proton transfer from acid to amine is complete to give salts, the basic structural motif is a three-component centrosymmetric aggregate, anion–cation–anion, in which the components are linked by N—H···O hydrogen bonds. Since there is an excess of hydrogen-bond acceptors, in the form of the four nitro groups per aggregate, over hard hydrogen-bond donors, C—H···O hydrogen bonds are formed which link the finite three-component aggregates into continuous arrays, which can be one-, two- or three-dimensional, as exemplified by the adducts formed by *N,N,N′,N′*-tetramethyl-1,2-diaminoethane (Me₂NCH₂CH₂-NMe₂), 1,4-diazabicyclo[2.2.2]octane [N(CH₂CH₂)₃N] and *N,N′*-dimethylpiperazine [MeN(CH₂CH₂)₂NMe], respectively.

Seeking to develop analogous systems in which the acid component contains instead an excess of soft hydrogen-bond donors over acceptors, we have now turned to ferrocenecarboxylic acid [FcCOOH = (C₅H₅)Fe(C₅H₄COOH)] as the

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acid component, and we report here the structure of its 2:1 adduct, (I), with 1,4-diazabicyclo[2.2.2]octane (DABCO).


(I)
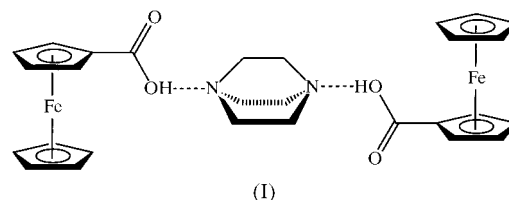
Cocrystallization of FcCOOH with DABCO provides the 2:1 adduct $2C_{11}H_{10}FeO_2\cdot C_6H_{12}N_2$, as expected, in which the three-molecular components within the asymmetric unit (Fig. 1) are linked by two O—H···N hydrogen bonds, rather than by N—H···O hydrogen bonds as in the corresponding adduct formed by 3,5-dinitrobenzoic acid (Burchell, Glidewell *et al.*, 2001). These two hydrogen bonds both have very short O···N distances, associated with nearly linear O—H···N arrays (Table 2); it may thus be deduced that these hydrogen bonds are strong for their types. Consistent with the short O···N distances, the O—H distances (Table 2) are somewhat longer than those normally found in carboxylic acids; in general, short *D*···*A* distances are associated with long *D*—H distances, culminating in very short *D*···*A* distances having approximately centred H atoms (Emsley, 1980; Aakeröy & Seddon, 1993). The marked difference between the C—O and C=O bond lengths is consistent with the neutral character of all the molecular components.

Apart from the C and H atoms of DABCO, the three-component aggregate (Fig. 1) is close to being centrosymmetric; indeed the ferrocene units alone form an almost centrosymmetric array, corresponding to a *P*2₁/*c* structure whose unit cell can be generated from the observed cell by the transformation (½0½/010/$\overline{1}$00). The fully ordered nature of the DABCO unit in (I) precludes the occurrence of any additional symmetry. It is, however, necessary to note here that DABCO has been observed (Ferguson *et al.*, 1998) disordered across a centre of inversion in the 1:1 adduct with 4,4′-biphenol. It is possible that in that adduct, the disordered model deduced from the X-ray diffraction data is, in fact, a static representation of a dynamic system, where the C-atom sites correspond to local minima in the rotation of the DABCO unit around its N···N vector. Such a motion, consisting of 60° jumps, would be prevented in compound (I) by the C—H···O hydrogen bonds formed by the DABCO component (see below).
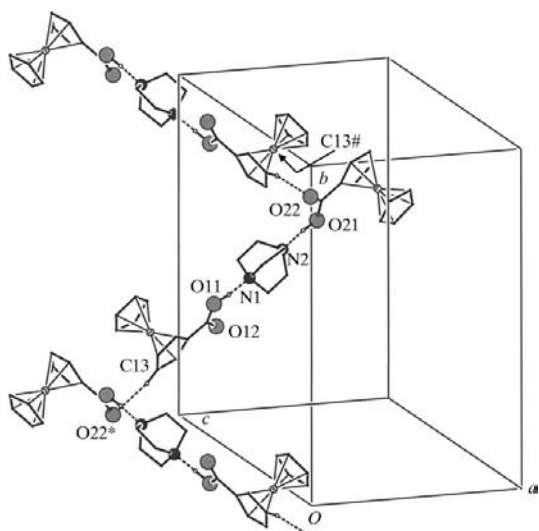
In the FcCOOH components, there are no significant differences in either the Fe—C distances or in the ring C—C distances, either between the two independent units or between the two types of ring, substituted and unsubstituted. In each FcCOOH molecule, the two rings are almost fully eclipsed: the mean values of the C—C*g*(*A*)—C*g*(*B*)—C torsion angles [where C*g*(*A*) and C*g*(*B*) represent the centroids of the two rings in that molecule] are 2.1 (2)° in molecule 1 (containing Fe1) and 0.4 (2)° in molecule 2 (containing Fe2), and the corresponding C*g*—Fe—C*g* angles are 177.65 (11) and 178.36 (10)°. In each molecule, the

metal-organic compounds
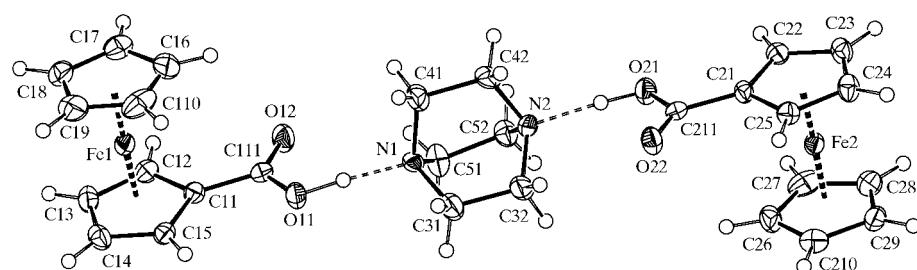
Figure 1
The asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

carboxyl substituent is essentially coplanar with the adjacent ring, with these groups twisted out of the plane of the adjacent ring by 3.3 (2) and 6.3 (2)° in molecules 1 and 2, respectively. The DABCO component shows the usual twist (Table 1) from idealized D_{3h} ($\bar{6}m2$) symmetry to D_3 (32) consequent upon the
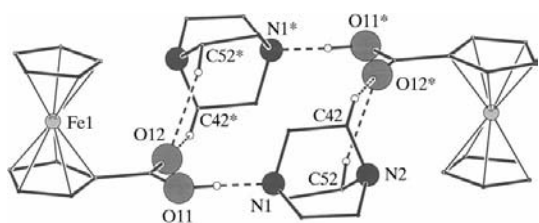
eclipsing of the C—H bonds which is required in the D_{3h} conformation. Despite the shortness of the O—H···N hydrogen bonds discussed earlier, the C—N distances, mean value 1.477 (5) Å, are typical of those in unprotonated DABCO units. For comparison, in the two independent monoprotonated [H(DABCO)]$^+$ units in the 3,5-dihydroxybenzoate salt (Burchell, Ferguson *et al.*, 2001), the C—N bonds at the unprotonated N have a mean value of 1.473 (3) Å, with a range of 1.466 (3)–1.480 (2) Å, while those at the protonated N have a mean value of 1.493 (3) Å, with a range of 1.486 (2)–1.498 (2) Å.

The three-component aggregates are linked into continuous sheets by means of C—H···O hydrogen bonds (Table 2), in which the carbonyl O atoms O12 and O22 (Fig. 1) act as the acceptors. Ferrocene C13 at $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$ acts as hydrogen-bond donor to O22 at (x, y, z), while C13 at (x, y, z) in turn acts as hydrogen-bond donor to O22 at $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$, so generating a $C_3^3(15)$ spiral chain around the 2_1 screw axis along $(0, y, \frac{3}{4})$ (Fig. 2). A second spiral chain of this type, related to the first by the centres of inversion and thus running anti-parallel to it, lies around the 2_1 axis along $(0, y, \frac{1}{4})$. These spiral chains are linked to form sheets by paired C—H···O hydrogen bonds. Atoms C42 and C52 in the DABCO unit at (x, y, z) both act as hydrogen-bond donors, *via* H42*A* and H52*B*, respectively, to O12 at $(-x, 1 - y, 1 - z)$; these two hydrogen bonds thus generate a local $R_2^1(6)$ ring, and propagation by the centre of inversion at $(0, \frac{1}{2}, \frac{1}{2})$ generates an $R_4^4(16)$ ring containing two FcCOOH and two DABCO units (Fig. 3). Each three-component aggregate is thus linked to three other such aggregates, two within a spiral chain along [010] and the third within the $R_4^4(16)$ ring; the combination of the $C_3^3(15)$ and $R_4^4(16)$ motifs thus generates a sheet parallel to (100) in the form of a (6,3) net (Batten & Robson, 1998) (Fig. 4).
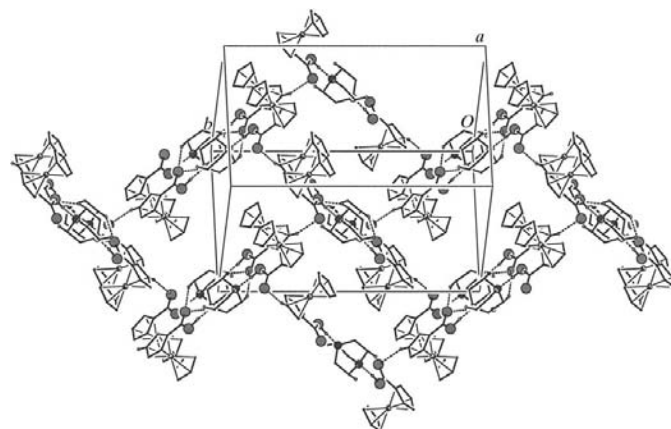

Figure 2
Part of the crystal structure of (I) showing the formation of a $C_3^3(15)$ spiral parallel to [010]. For the sake of clarity, H atoms not participating in the motif shown have been omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$ and $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively.

Figure 3
Part of the crystal structure of (I) showing the formation of a centrosymmetric $R_4^4(16)$ ring with $R_2^1(6)$ rings embedded. For the sake of clarity, H atoms not participating in the motif shown have been omitted. The atoms marked with an asterisk (*) are at the symmetry position $(-x, 1 - y, 1 - z)$.

Figure 4
Part of the crystal structure of (I) showing the formation of a (6,3) net parallel to (100).

Experimental

Stoichiometric quantities of FcCOOH and DABCO were separately dissolved in methanol. The solutions were mixed and the mixture was set aside to crystallize, producing analytically pure (I). Analysis, found: C 58.6, H 5.4, N 4.4%; $C_{28}H_{32}Fe_2N_2O_4$ requires: C 58.8, H 5.6, N 4.9%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$2[Fe(C_5H_5)(C_6H_5O_2)]\cdot C_6H_{12}N_2$	$D_x = 1.522$ Mg m^{-3}
$M_r = 572.26$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4385
$a = 11.3900$ (2) Å	reflections
$b = 21.2256$ (6) Å	$\theta = 2.8$–$25.0°$
$c = 11.7248$ (3) Å	$\mu = 1.20$ mm^{-1}
$\beta = 118.2144$ (12)°	$T = 150$ (2) K
$V = 2497.79$ (10) Å^3	Needle, orange
$Z = 4$	$0.18 \times 0.07 \times 0.06$ mm

Data collection

KappaCCD diffractometer	2722 reflections with $I > 2\sigma(I)$
φ and ω scans with κ offsets	$R_{int} = 0.10$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(DENZO–SMN; Otwinowski &	$h = 0 \rightarrow 13$
Minor, 1997)	$k = 0 \rightarrow 25$
$T_{min} = 0.813$, $T_{max} = 0.932$	$l = -13 \rightarrow 12$
4527 measured reflections	Intensity decay: negligible
4385 independent reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.044$	independent and constrained
$wR(F^2) = 0.104$	refinement
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2]$
4385 reflections	where $P = (F_o^2 + 2F_c^2)/3$
333 parameters	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.37$ e Å^{-3}
	$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C111—O12	1.229 (4)	C211—O22	1.220 (4)
C111—O11	1.320 (4)	C211—O21	1.330 (4)
N1—C31	1.474 (5)	N2—C32	1.477 (5)
N1—C41	1.471 (5)	N2—C42	1.477 (4)
N1—C51	1.476 (5)	N2—C52	1.487 (5)
C12—C11—C111—O11	175.8 (4)	N1—C31—C32—N2	8.0 (5)
C12—C11—C111—O12	−6.5 (7)	N1—C41—C42—N2	6.2 (5)
C22—C21—C211—O21	3.2 (6)	N1—C51—C52—N2	7.5 (4)
C22—C21—C211—O22	−175.3 (4)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O11—H1$\cdots$N1	1.06 (6)	1.53 (5)	2.578 (4)	170 (5)
O21—H2$\cdots$N2	0.99 (7)	1.62 (7)	2.604 (5)	174 (6)
C13—H13$\cdots$O22^i	0.95	2.51	3.401 (5)	157
C42—H42$A\cdots$O12^{ii}	0.99	2.44	3.327 (5)	149
C52—H52$B\cdots$O12^{ii}	0.99	2.49	3.369 (5)	149

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

Compound (I) crystallized in the monoclinic system; space group $P2_1/c$ was uniquely assigned from the systematic absences. H atoms bonded to C atoms were treated as riding atoms, with C—H = 0.95 (FcCOOH) and 0.99 Å (DABCO). Hydroxy H atoms H1 and H2 were refined isotropically.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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