

## Adducts of hexamethylenetetramine with ferrocenecarboxylic acid and ferrocene-1,1'-dicarboxylic acid: multiple disorder in space groups *Fmm2* and *Cmcm*

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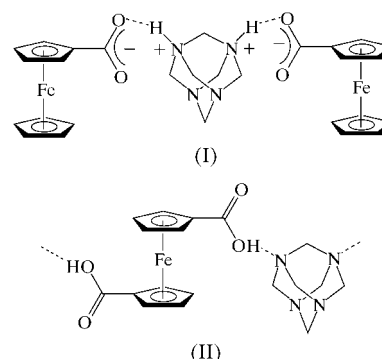
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Hexamethylenetetramine,  $C_6H_{12}N_4$ , and ferrocenecarboxylic acid,  $C_{11}H_{10}FeO_2$ , form a 1:2 adduct, (I), which is a salt, *viz.* hexamethylenetetraminium(2+) bis(ferrocenecarboxylate),  $(C_6H_{14}N_4)[Fe(C_5H_5)(C_6H_4O_2)]_2$ . The dication in (I) is disordered with two orientations at a site of *mm2* symmetry in space group *Fmm2*, while the anion lies across a mirror plane with its unsubstituted cyclopentadienyl ring disordered over two sets of sites. With ferrocene-1,1'-dicarboxylic acid,  $C_{12}H_{10}FeO_4$ , hexamethylenetetramine forms a 1:1 adduct, (II), in which both components are neutral, *viz.* hexamethylenetetramine-ferrocene-1,1'-dicarboxylic acid (1/1),  $[Fe(C_6H_5O_2)_2] \cdot C_6H_{12}N_4$ . The amine component in (II) is disordered with two orientations at a site of *mm2* symmetry in space group *Cmcm*, while the acid component is disordered with two orientations at a site of *2/m* symmetry. The components in (I) are linked into a finite three-ion aggregate by a single N—H...O hydrogen bond, while the components of (II) are linked into continuous chains by a single O—H...N hydrogen bond.

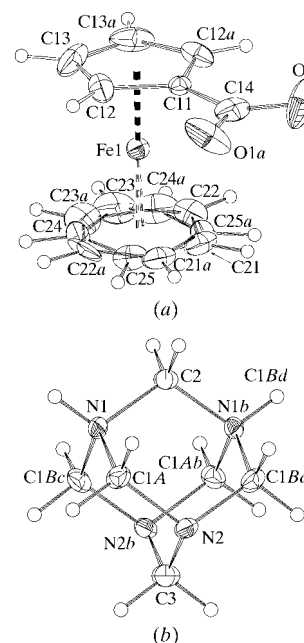
### Comment

The stoichiometric adducts formed between ferrocene-1,1'-dicarboxylic acid,  $[Fe(C_5H_4COOH)_2]$ , and a wide variety of amines are all salts, some of which contain the monoanion  $[Fe(C_5H_4COOH)(C_5H_4COO^-)]$  (Braga *et al.*, 2000, 2002; Zakaria *et al.*, 2002), and others of which contain the dianion  $[Fe(C_5H_4COO^-)_2]$  (Braga *et al.*, 2000, 2001; Zakaria *et al.*, 2002). On the other hand, the sole such adduct reported to date formed by ferrocenecarboxylic acid,  $[(C_5H_5)Fe(C_5H_4-$

COOH)], is the 1:2 adduct formed with the cage-type diamine 1,4-diazabicyclo[2.2.2]octane ( $C_6H_{12}N_2$ , DABCO), which contain two neutral components, *viz.*  $C_6H_{12}N_2 \cdot 2C_{11}H_{10}FeO_2$ , linked by O—H...N hydrogen bonds (Zakaria *et al.*, 2001). By contrast, the adduct formed between DABCO and ferrocene-1,1'-dicarboxylic acid is the salt  $[(C_6H_{12}N_2)H]^+ \cdot [Fe(C_5H_4COOH)(C_5H_4COO^-)]^-$ , in which the components are linked into chains by a combination of N—H...O and O—H...N hydrogen bonds (Zakaria *et al.*, 2002; Braga *et al.*, 2002).



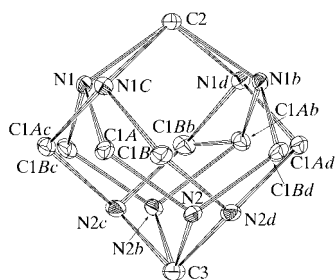
We have now investigated the adducts formed by the same two ferrocene acids with a second cage-type amine, *viz.* hexamethylenetetramine ( $C_6H_{12}N_4$ , HMTA), where we find a reversal of the behaviour observed in the corresponding DABCO adducts. With HMTA, ferrocenecarboxylic acid forms a salt-type 1:2 adduct  $[(C_6H_{12}N_4)H_2]^{2+} \cdot [Fe(C_5H_4COOH)(C_5H_4COO^-)]_2$ , (I), containing the uncommon diprotonated form of HMTA, while ferrocene-1,1'-dicarboxylic acid forms



**Figure 1**

The independent components of compound (I), showing the atom-labelling scheme, for (a) the anion, where atoms marked with suffix 'a' are at the symmetry position  $(1-x, y, z)$ , and (b) one orientation of the cation, where atoms marked with suffixes 'b', 'c' and 'd' are at the symmetry positions  $(1-x, -y, z)$ ,  $(1-x, y, z)$  and  $(x, -y, z)$ , respectively. Displacement ellipsoids are drawn at the 30% probability level.

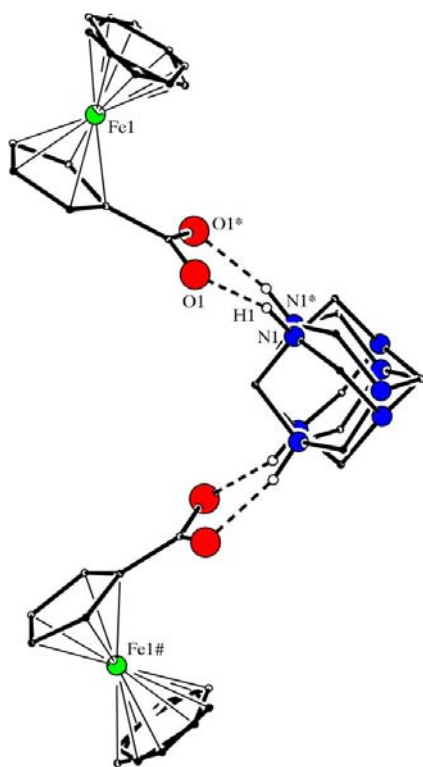
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**Figure 2**  
The two alternative orientations of the cation in compound (I). The atoms are labelled as in Fig. 1(b) and H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level.

a 1:1 adduct, (II), in which both components are neutral, thus  $C_6H_{12}N_4 \cdot [Fe(C_5H_4COOH)_2]$ .

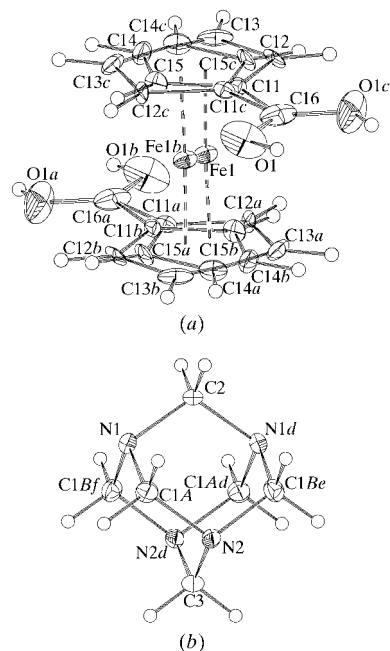
In the salt (I), the anion lies across a mirror plane in space group  $Fmm2$ , selected for the reference anion as that at  $x = \frac{1}{2}$ . The Fe atom and the substituted cyclopentadienyl ring are fully ordered, but the unsubstituted ring is disordered over two sets of sites both having an occupancy of 0.5 (Fig. 1a). The cation is at a site of  $mm2$  ( $C_{2v}$ ) symmetry, with atoms C2 and C3 (Fig. 1b) lying fully ordered on the twofold axis along  $(\frac{1}{2}, 0, z)$ ; all the other non-H atoms of the cation are disordered over two sets of sites related by the mirror planes at  $x = \frac{1}{2}$  and  $y = 0$ . Hence the two alternative orientations of the HMTA cage appear to be intimately interwoven (Fig. 2).



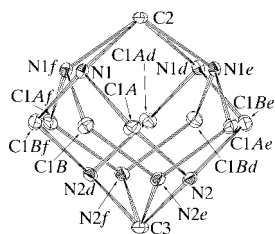
**Figure 3**  
Part of the crystal structure of (I), showing the formation of a three-component aggregate by means of a single  $N-H \cdots O$  hydrogen bond. For the sake of clarity, the unit-cell box and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (\*) or hash (#) are at the symmetry positions  $(1-x, y, z)$  and  $(\frac{1}{2}, -y, z)$ , respectively.

The bond distances in the anion of (I) show no unexpected features. In the cation, the ranges of the C–N distances involving protonated atom N1 and unprotonated atom N2 overlap (Table 1), and there is no significant difference between the mean values for the two types. By contrast, in the monoprotonated HMTA cation,  $[(C_6H_{12}N_4)H]^+$ , it is possible to discern three distinct ranges of C–N distances, which indicate considerable progress along the acid-induced decomposition pathway which leads eventually to complete break-up of the HMTA cage (Lough *et al.*, 2000). This diprotonated HMTA dication is unusual, and only one other example is recorded in the February 2003 release of the Cambridge Structural Database (CSD; Allen, 2002). In this example, containing a polymolybdate anion, *viz.*  $2Na^+ \cdot 2[(C_6H_{12}N_4)H_2]^{2+} \cdot [Mo_7O_{24}]^{6-} \cdot 9H_2O$  (CSD refcode XOXQOQ; Yang *et al.*, 2002), no H-atom coordinates were reported nor is it clear how the H atoms were located. Nevertheless, two of the four N atoms of the HMTA cage in XOXQOQ are within hydrogen-bonding distance of an O atom.

The component ions of (I) are linked by a single  $N-H \cdots O$  bond (Table 2), forming a finite three-component aggregate (Fig. 3), but there are neither  $C-H \cdots X$  or  $X-H \cdots \pi$  (cyclopentadienyl) ( $X = N$  or  $O$ ) interactions between these aggregates. By contrast, in the analogous DABCO adduct, the three-component aggregates are linked into sheets by a series of  $C-H \cdots O$  hydrogen bonds (Zakaria *et al.*, 2001).

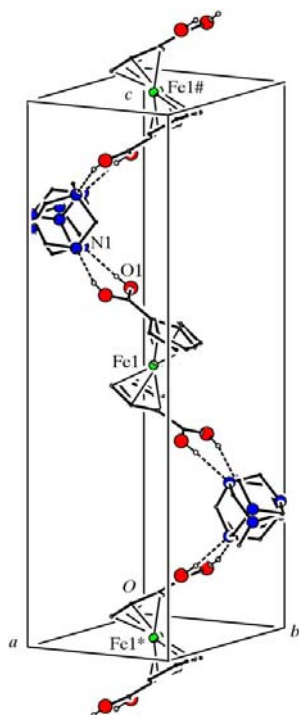


**Figure 4**  
The independent components of compound (II), showing the atom-labelling scheme, for (a) the disordered acid component, where atoms marked with suffixes 'a', 'b' and 'c' are at the symmetry positions  $(x, 1-y, 1-z)$ ,  $(1-x, 1-y, 1-z)$  and  $(1-x, y, z)$ , respectively, and (b) one orientation of the amine, where atoms marked with suffixes 'd', 'e' and 'f' are at the symmetry positions  $(1-x, y, \frac{3}{2}-z)$  ( $x, y, \frac{3}{2}-z$ ) and  $(1-x, y, z)$ , respectively. Displacement ellipsoids are drawn at the 30% probability level.


**Figure 5**

The two alternative orientations of the amine molecule in compound (II). The atoms are labelled as in Fig. 4(b) and H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level.

The acid component of compound (II) lies at a site of  $2/m$  ( $C_{2h}$ ) symmetry in space group  $Cmcm$ , selected as that at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , and it is disordered over two sets of sites related by mirror symmetry such that only the carboxyl atom C16 is common to the two orientations (Fig. 4a). An individual molecule of the acid component therefore exhibits only twofold rotational symmetry. The neutral amine component of (II), like the cation in (I), lies at a site of  $mm2$  ( $C_{2v}$ ) symmetry, with atoms C2 and C3 lying on the twofold axis along  $(\frac{1}{2}, y, \frac{3}{4})$  (Fig. 4b). The amine is disordered over two sets of sites related by the mirror plane at  $x = \frac{1}{2}$  (Fig. 5), so that its behaviour is very similar to that of the cation in (I). Again there is no significant difference between the two types of C–N bond distance (Table 3), namely those involving N1, the acceptor of the O–H $\cdots$ N hydrogen bond, and those involving N2, which is not a hydrogen-bond acceptor. As in compound (I), a single


**Figure 6**

Part of the crystal structure of (II), showing the formation of a [001] chain by means of a single O–H $\cdots$ N hydrogen bond. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (\*) or hash (#) are in the acid components centred at  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, 1)$ , respectively.

hydrogen bond (Table 4) links the components of (II), forming a  $C(12)$  chain (Bernstein *et al.*, 1995) running parallel to the [001] direction (Fig. 6). In the corresponding DABCO adduct, the chains formed by the ionic components are linked into sheets by C–H $\cdots$ O hydrogen bonds (Zakaria *et al.*, 2002).

## Experimental

Stoichiometric quantities of HMTA and the appropriate acid were separately dissolved in tetrahydrofuran; the solutions of amine and acid were mixed and the mixtures were then set aside to crystallize, producing analytically pure samples of (I) and (II). Analysis found for (I): C 56.4, H 5.0, N 9.3%;  $C_{28}H_{32}Fe_2N_4O_4$  requires: C 56.0, H 5.4, N 9.3%; found for (II): C 51.7, H 5.4, N 13.3%;  $C_{18}H_{22}FeN_4O_4$  requires: C 52.2, H 5.4, N 13.5%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

## Compound (I)

### Crystal data

$(C_6H_{14}N_4)[Fe(C_5H_5)(C_6H_4O_2)]_2$   
 $M_r = 600.28$   
 Orthorhombic,  $Fmm2$   
 $a = 9.9496(8) \text{ \AA}$   
 $b = 36.295(3) \text{ \AA}$   
 $c = 7.0643(6) \text{ \AA}$   
 $V = 2551.1(4) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.563 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 1351 reflections  
 $\theta = 2.6\text{--}27.4^\circ$   
 $\mu = 1.18 \text{ mm}^{-1}$   
 $T = 150(1) \text{ K}$   
 Block, orange  
 $0.28 \times 0.26 \times 0.22 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  scans, and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)  
 $T_{\min} = 0.709$ ,  $T_{\max} = 0.775$   
 2539 measured reflections

1351 independent reflections  
 1197 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.055$   
 $\theta_{\max} = 27.4^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -46 \rightarrow 45$   
 $l = -8 \rightarrow 8$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.099$   
 $S = 1.06$   
 1351 reflections  
 129 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + 2.01P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.32 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0031 (6)  
 Absolute structure: Flack (1983),  
 507 Friedel pairs  
 Flack parameter = 0.33 (4)

**Table 1**

Selected interatomic distances ( $\text{\AA}$ ) for (I).

N1–C1A	1.484 (10)	N2–C1A	1.484 (10)
N1–C1B <sup>i</sup>	1.489 (9)	N2–C1B <sup>ii</sup>	1.438 (10)
N1–C2	1.461 (7)	N2–C3	1.465 (8)

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

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ ) for (I).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1–H1 $\cdots$ O1	0.93	1.87	2.770 (6)	162

**Table 3**

Selected interatomic distances (Å) for (II).

N1—C1A	1.492 (6)	N2—C1A	1.467 (6)
N1—C1B <sup>i</sup>	1.481 (7)	N2—C1B <sup>ii</sup>	1.469 (6)
N1—C2	1.483 (4)	N2—C3	1.476 (4)

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

## Compound (II)

### Crystal data

 $[\text{Fe}(\text{C}_6\text{H}_5\text{O}_2)_2] \cdot \text{C}_6\text{H}_{12}\text{N}_4$ 
 $M_r = 414.25$ 

 Orthorhombic, *Cmcm*
 $a = 10.0096$  (4) Å

 $b = 7.1396$  (2) Å

 $c = 24.2841$  (8) Å

 $V = 1735.45$  (10) Å<sup>3</sup>
 $Z = 4$ 
 $D_x = 1.585$  Mg m<sup>-3</sup>

 Mo  $K\alpha$  radiation

Cell parameters from 895

reflections

 $\theta = 2.6$ – $25.0^\circ$ 
 $\mu = 0.90$  mm<sup>-1</sup>
 $T = 150$  (1) K

Plate, orange

 $0.28 \times 0.25 \times 0.06$  mm

### Data collection

Nonius KappaCCD diffractometer

 $\varphi$  scans, and  $\omega$  scans with  $\kappa$  offsets

Absorption correction: multi-scan

 (*DENZO-SMN*; Otwinowski & Minor, 1997)

 $T_{\min} = 0.786$ ,  $T_{\max} = 0.948$ 

6092 measured reflections

836 independent reflections

 671 reflections with  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.045$ 
 $\theta_{\text{max}} = 25.0^\circ$ 
 $h = 0 \rightarrow 11$ 
 $k = 0 \rightarrow 8$ 
 $l = -28 \rightarrow 0$ 

### Refinement

 Refinement on  $F^2$ 
 $R[F^2 > 2\sigma(F^2)] = 0.032$ 
 $wR(F^2) = 0.073$ 
 $S = 1.13$ 

836 reflections

103 parameters

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0024P)^2 + 3.0941P]$ 

 where  $P = (F_o^2 + 2F_c^2)/3$ 
 $(\Delta/\sigma)_{\text{max}} < 0.001$ 
 $\Delta\rho_{\text{max}} = 0.27$  e Å<sup>-3</sup>
 $\Delta\rho_{\text{min}} = -0.45$  e Å<sup>-3</sup>

Crystals of both (I) and (II) are orthorhombic. For (I), the systematic absences permitted *F222*, *Fmm2* and *Fmmm* as possible space groups, but only *Fmm2* allowed a successful refinement, with both the  $\text{C}_{11}\text{H}_9\text{FeO}_2$  and  $\text{C}_6\text{H}_{14}\text{N}_4$  moieties being disordered. Cyclopentadienyl ring C21–C25 is disordered and was allowed for using the *SHELXL97* (Sheldrick, 1997) AFIX 59 command during the refinement. There was no evidence for an H atom being bonded to O1, but there was some residual density adjacent to N1 directed towards O1; accordingly, the *SHELXL97* HFIX 13 command was used to generate a riding H atom on N1, with an N–H distance of 0.93 Å. For (II), the systematic absences permitted *Cmc21*, *C2cm* (= *Ama2*, No. 40) and *Cmcm* as possible space groups, but only *Cmcm* allowed a successful refinement, with both the  $\text{C}_{12}\text{H}_{10}\text{FeO}_4$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  moieties being disordered. Investigation of the *Cmc21* and *C2cm* possibilities led to refinements with rather higher *R* values than the *Cmcm* refinement, despite the greater number of parameters; for these refinements, the *ADDSYM* option in *PLATON* (Spek, 2003) reported a 100% fit for space group *Cmcm*. However, we emphasize that regardless of which one of these space groups is considered, the overall structure is unchanged. There was no evidence for an H atom being bonded to N1, but there was some residual density adjacent to O1 directed towards N1; accordingly the *SHELXL97* HFIX 147

**Table 4**

Hydrogen-bonding geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 $\cdots$ N1	0.84	1.97	2.786 (3)	165

command was used to generate a riding H atom on O1, with an O–H distance of 0.84 Å. In both structures, all H atoms bonded to C atoms were identified in difference maps and were treated as riding atoms, with C–H distances of 0.95 Å (cyclopentadienyl) or 0.99 Å ( $\text{CH}_2$ ). For compound (I), the Flack (1983) parameter of 0.33 (4) indicated racemic twinning.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; 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: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada. CMZ thanks the Association of Commonwealth Universities for the award of a Commonwealth Fellowship 2000–2001.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1641). Services for accessing these data are described at the back of the journal.

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