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Hydrogen-bonded adducts of ferrocene-1,1′-diylbis(diphenylmethanol): monomeric and polymeric adducts with 1,2-bis(4-pyridyl)ethene and 1,6-diaminohexane

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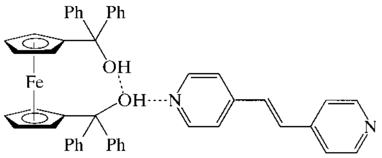
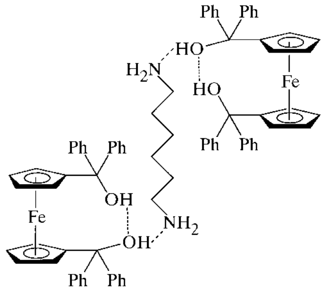
In the adduct ferrocene-1,1′-diylbis(diphenylmethanol)–1,2-bis(4-pyridyl)ethene (1/1), $[Fe(C_{18}H_{15}O)_2]\cdot C_{12}H_{10}N_2$, there is an intramolecular O—H···O hydrogen bond in the ferrocenediol component and a single O—H···N hydrogen bond linking the diol to the diamine, which is disordered over two sets of sites, so forming a finite monomeric adduct. In the adduct ferrocene-1,1′-diylbis(diphenylmethanol)–1,6-diaminohexane (2/1), $2[Fe(C_{18}H_{15}O)_2]\cdot C_6H_{16}N_2$, the amine lies across a centre of inversion in space group $P\overline{1}$. There is an intramolecular O—H···O hydrogen bond in the ferrocenediol, and the molecular components are linked by O—H···N and N—H···O hydrogen bonds, one of each type, into a $C_3^3(13)[R_6^6(12)]$ chain of rings.

Comment

The organometallic diol ferrocene-1,1′-diylbis(diphenylmethanol), $[Fe(C_5H_4CPh_2OH)_2]$, forms a 1:1 hydrogen-bonded adduct with 4,4′-bipyridyl in which only half of the bipyridyl molecules are involved in the supramolecular aggregation; this takes the form of a finite centrosymmetric three-component diol–diamine–diol aggregate, while the remainder of the bipyridyl molecules occupy isolated sites within the structure (Glidewell *et al.*, 1994). By contrast, the 1:1 adduct formed by this diol with 1,2-bis(4-pyridyl)ethane crystallizes as a finite monomeric adduct in which one of the N atoms plays no part in the hydrogen bonding (Zakaria *et al.*, 2001). The 1:1 adduct formed by the ferrocenediol with 1,2-diaminoethane, by contrast, exhibits a much more complex structure, in the form of two independent four-molecule aggregates, $(diol)_2\cdot(diamine)_2$, both of which are centrosymmetric, but which exhibit different patterns of hydrogen bonds (Zakaria *et al.*, 2001). Continuing this theme, we have now synthesized and structurally characterized two further adducts with related diamines, *viz.* the 1:1 adduct with *trans*-1,2-bis(4-pyridyl)ethene, $[Fe(C_{18}H_{15}O)_2]\cdot C_{12}H_{10}N_2$, (I), and the 2:1 adduct with 1,6-diaminohexane (systematic name: hexane-1,6-diamine), $2[Fe(C_{18}H_{15}O)_2]\cdot C_6H_{16}N_2$, (II).



(I)



(II)

Compound (I) consists of finite 1:1 aggregates (Fig. 1); in addition to an intermolecular O—H···O hydrogen bond within the diol (Table 2), there is an O—H···N hydrogen bond linking the molecular components. By contrast with the fully ordered diamine in the analogous 1,2-bis(4-pyridyl)ethane adduct, in (I), the 1,2-bis(4-pyridyl)ethene molecules exhibit orientational disorder over two sets of sites of a type previously observed in the 1:1 adduct of this diamine with 4,4′-sulfonyldiphenol (Ferguson *et al.*, 1999). The two sets of sites, whose refined site-occupation factors are 0.601 (5) and 0.399 (5), can be most simply envisaged as resulting from a 180° rotation about a line which approximates to the N···N vector, so that the heteroaromatic ring positions are similar in the two orientations, but the two central C═C bonds are nearly orthogonal. In neither orientation of the diamine does the remote N atom act as a hydrogen-bond acceptor.

In compound (II) (Fig. 2), the 1,6-diaminohexane component lies across a centre of inversion in space group $P\overline{1}$, selected for the sake of convenience as that at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, while the ferrocenediol lies in a general position. There is the usual intramolecular O—H···O hydrogen bond within the ferrocenediol, and the free hydroxyl group forms an O—H···N hydrogen bond with the amine (Table 4); a centrosymmetric three-molecule diol–diamine–diol aggregate thus results. In addition, the amino N1 atom at (x, y, z), which is a component of the three-molecule aggregate centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, acts as a hydrogen-bond donor, *via* H1*A*, to O1 at $(2 - x, 1 - y, 1 - z)$, which is a component of the aggregate centred at $(\frac{3}{2},\frac{1}{2},\frac{1}{2})$; N1 at $(2 - x, 1 - y, 1 - z)$, in turn, acts as donor to O1 at (x, y, z),

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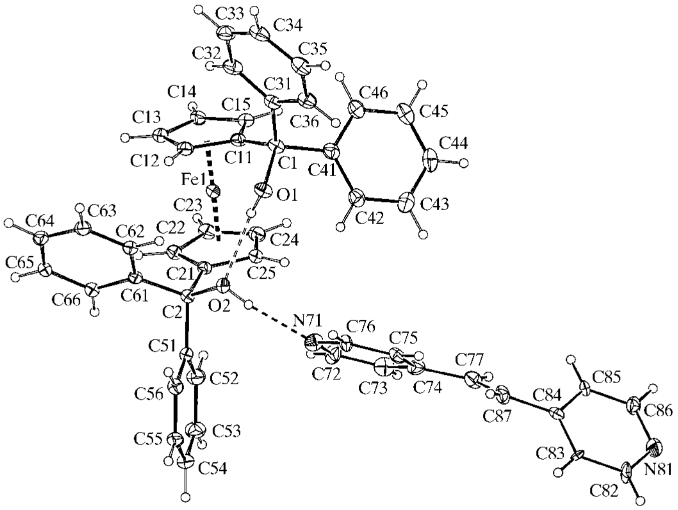

Figure 1
View of the molecular aggregate in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only the major orientation of the diamine is shown.

producing a centrosymmetric $R^6_6(12)$ ring centred at $(1,\frac{1}{2},\frac{1}{2})$. The symmetry-related N1 atom in the aggregate centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is at $(1 - x, 1 - y, 1 - z)$, and this acts as a hydrogen-bond donor to O1 at $(-1 + x, y, z)$, part of the aggregate centred at $(-\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Propagation of this N—H···O hydrogen bond thus generates a $C^3_3(13)[R^6_6(12)]$ chain of rings running parallel to the [100] direction; in this chain, the $R^6_6(12)$ rings are centred at $(n, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer), while the diamines linking the $R^6_6(12)$ rings are centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer) (Fig. 3). The second H atom of the amino group, H1*B*, plays no role in the hydrogen bonding.

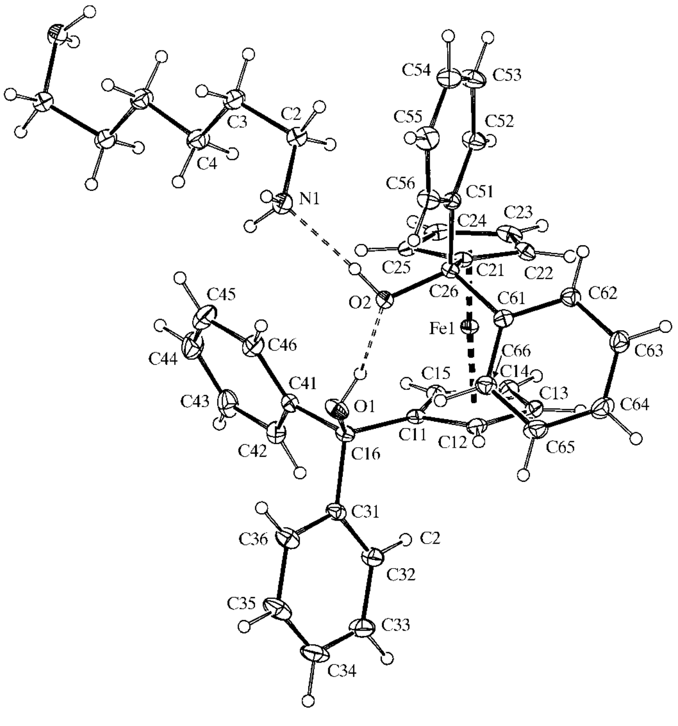

Figure 2
View of the molecular components of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The pairwise linking of the ferrocenediol molecules into centrosymmetric $R^6_6(12)$ rings by pairs of *X*—H units, which can act as both donors and acceptors of hydrogen bonds, observed here for *X* = N, has also been observed in the finite 1:1 adduct formed between the ferrocenediol and methanol, when *X* = O (Ferguson *et al.*, 1993). The overall ribbon-like structure of (II) has the hydrogen-bonded rings along the centre of the ribbon, with the ferrocenyl and phenyl units on the periphery. This arrangement effectively precludes the formation of any hydrogen bonds, hard or soft, between adjacent chains, and thus possibly accounts for the non-participation in the hydrogen bonding of H1*B*. In much the same way, in the finite zero-dimensional aggregates formed in the adduct of the ferrocenediol with 1,2-diaminoethane, the polar hydrogen-bonded core of each aggregate is prevented by the lipophilic organic substituents from interaction with the polar cores of adjacent aggregates.

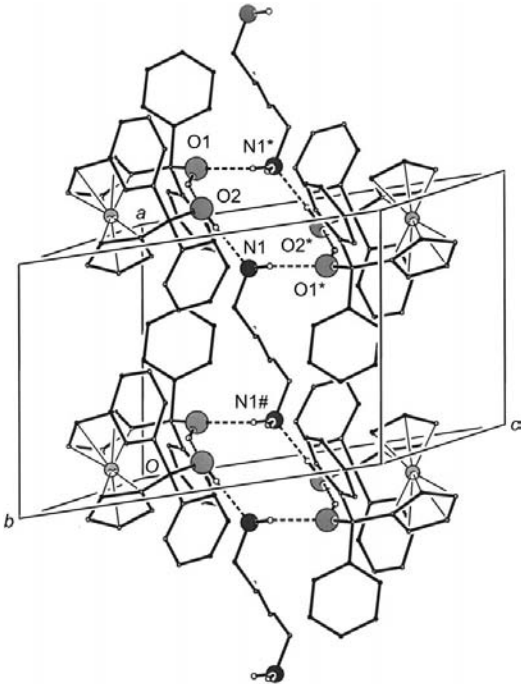

Figure 3
Part of the crystal structure of (II), showing the formation of a $C^3_3(13)[R^6_6(12)]$ chain of rings along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(2 - x, 1 - y, 1 - z)$ and $(1 - x, 1 - y, 1 - z)$, respectively.

In compound (I), both components of the amine are significantly non-planar (Table 1), and in compound (II), the terminal N—C—C—C fragment of the amine does not adopt the *trans*-planar conformation observed for the C—C—C—C fragments (Table 3). The bond lengths and angles show no unexpected features.

Experimental

For each adduct, equimolar quantities of the ferrocenediol and the appropriate diamine were separately dissolved in methanol. The component solutions were mixed and the mixtures set aside to crystallize, producing analytically pure (I) and (II). Analyses, compound (I): found C 78.7, H 5.3, N 3.7%; $C_{48}H_{40}FeN_2O_2$ requires C 78.7, H 5.5, N 3.8%; compound (II): found C 76.4, H 6.4, N 2.3%; $C_{78}H_{76}Fe_2N_2O_4$ requires C 77.0, H 6.3, N 2.3%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

Compound (I)

Crystal data

$[Fe(C_{18}H_{15}O)_2]\cdot C_{12}H_{10}N_2$
$M_r = 732.67$
Triclinic, $P\overline{1}$
$a = 9.6393$ (4) Å
$b = 11.4219$ (5) Å
$c = 17.7338$ (10) Å
$\alpha = 76.7680$ (18)°
$\beta = 87.4580$ (17)°
$\gamma = 74.064$ (3)°
$V = 1827.24$ (15) Å^3
$Z = 2$
$D_x = 1.332$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6061 reflections
$\theta = 2.6$–$25.0°$
$\mu = 0.46$ mm^{-1}
$T = 150$ (2) K
Block, orange
0.23 × 0.16 × 0.14 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.902$, $T_{max} = 0.939$
16 969 measured reflections
6460 independent reflections
4709 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = -20 \rightarrow 21$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.125$
$S = 1.03$
6460 reflections
526 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 1.2945P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0044 (10)

Table 1
Selected torsion angles (°) for (I).

C73—C74—C77—C87	−161.5 (6)
C75—C74—C77—C87	17.1 (10)
C83—C84—C87—C77	−139.5 (6)
C85—C84—C87—C77	41.2 (8)
C73*A*—C74*A*—C77*A*—C87*A*	31.1 (18)
C75*A*—C74*A*—C77*A*—C87*A*	−152.3 (13)
C83*A*—C84*A*—C87*A*—C77*A*	10.8 (16)
C85*A*—C84*A*—C87*A*—C77*A*	−176.5 (11)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.84	2.05	2.787 (3)	147
O2—H2···N71	0.84	1.96	2.786 (4)	168

Compound (II)

Crystal data

$2[Fe(C_{18}H_{15}O)_2]\cdot C_6H_{16}N_2$
$M_r = 1217.11$
Triclinic, $P\overline{1}$
$a = 10.2027$ (2) Å
$b = 11.7067$ (2) Å
$c = 14.6172$ (3) Å
$\alpha = 84.9780$ (9)°
$\beta = 70.2454$ (8)°
$\gamma = 70.3612$ (8)°
$V = 1546.88$ (5) Å^3
$Z = 1$
$D_x = 1.307$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6769 reflections
$\theta = 3.0$–$27.6°$
$\mu = 0.52$ mm^{-1}
$T = 150$ (2) K
Block, orange
0.40 × 0.30 × 0.28 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.818$, $T_{max} = 0.867$
23 031 measured reflections
7106 independent reflections
6398 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.6°$
$h = 0 \rightarrow 13$
$k = -13 \rightarrow 15$
$l = -17 \rightarrow 19$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.082$
$S = 1.03$
7106 reflections
391 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.7055P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 3
Selected torsion angles (°) for (II).

N1—C2—C3—C4	−61.89 (18)	C2—C3—C4—C4^i	−172.22 (16)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.84	2.09	2.8021 (13)	142
O2—H2···N1	0.84	1.91	2.7499 (16)	176
N1—H1*A*···O1^i	0.91	2.18	3.0669 (16)	166

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

Compounds (I) and (II) both crystallize in the triclinic system; for each, space group $P\overline{1}$ was assumed and subsequently confirmed by the analysis. In compound (I), the amine component is disordered over two sets of sites; the minor component was refined with a common isotropic displacement parameter for all the C and N atoms. All H atoms were treated as riding, with C—H = 0.95–0.99 Å, N—H = 0.91 Å and O—H = 0.84 Å.

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: *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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1515). Services for accessing these data are described at the back of the journal.

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