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Hydrogen-bonded adducts of ferrocene-1,1′-diylbis(diphenylmethanol) with nitrogenous bases: crystal and molecular structure of the 2:1 adduct with hexamethylenetetramine

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Abstract

Ferrocene-1,1′-diylbis(diphenylmethanol), $[Fe(C_5H_4CPh_2OH)_2]$ forms hydrogen-bonded host–guest adducts with nitrogenous bases. A 2:1 adduct is formed with hexamethylenetetramine, $[(CH_2)_6N_4]$, 1:1 adducts with 1,4-dimethylpiperazine and 1,4-diazabicyclo [2.2.2]octane and a 1:2 adduct with 3-pyridylferrocene. The crystal structure of the hexamethylenetetramine adduct has been determined. The structural unit contains two molecules of the host ferrocenediol and one molecule of the guest: the diol forms both intramolecular O–H ··· O and intermolecular O–H ··· N hydrogen bonds, but two of the four nitrogen atoms in the $[(CH_2)_6N_4]$ guest molecules play no part in the hydrogen bonding.

Keywords: Iron; Ferrocene; Host–guest adducts; Hydrogen bonding; Crystal structure

1. Introduction

The ferrocenediol ferrocene-1,1′-diylbis(diphenylmethanol), $[Fe(C_5H_4CPh_2OH)_2]$ **1**, forms hydrogen-bonded host-guest adducts with a wide range of oxygen- and nitrogen-containing guests [1,2]. A common feature of the hydrogen-bonding in these adducts is the formation of intramolecular O–H ··· O hydrogen bonds by the ferrocenediol, in addition to intermolecular O–H ··· N or O–H ··· O hydrogen bonds: such a pattern is found in the adducts formed by **1** with pyridine, 4,4′-bipyridyl, 1,4-dioxane, morpholine, methanol and dimethylformamide [1,2], as well as in **1** itself and a number of other related ferrocenediols [3]. The sole exception to this pattern found to date is for the adduct of **1** with piperazine [2], in which there are only intermolecular O–H ··· N hydrogen bonds: a plausible inference from the patterns [2] of hydrogen bonds observed in the host-guest adducts of **1** is that intermolecular O–H ··· N (aliphatic) hydrogen bonds are preferred over intramolecular O–H ··· O hydrogen bonds, but that such intramolecular hydrogen bonds are comparable in strength with both intermolecular O–H ··· N (aromatic) and intermolecular O–H ··· O=C$\langle$ hydrogen bonds.

In part, as a test of this idea, we have now investigated the behaviour of **1** as a host towards a range of aliphatic secondary and tertiary amines, as well as towards some aromatic nitrogen bases. As found previously [2], for none of these adducts can a structure be reliably predicted from knowledge of all the other structures.

2. Experimental details

Published methods were used for the preparation of ferrocene-1,1′-diylbis(diphenylmethanol) [1], 3-pyridylferrocene [4], 2-nitrophenylferrocene [5], 1,1′-bis(2-nitrophenyl)ferrocene [5], 4-nitrophenylferrocene [5], 2-aminophenylferrocene [5], 4-aminophenylferrocene [5] and bis(dimethylamino)methane [6]. Other amines were purchased; solid amines were used as received, and liquid amines were dried and purified by conventional methods [7]. Diethyl ether and light petroleum (b.p. 40–60°C) were dried by refluxing over sodium diphenylketyl, dichloromethane by refluxing over calcium hydride. Elemental analysis was by the Microanalytical Laboratory of this School. Proton and ^{13}C NMR spectra were recorded at 300.133 MHz and 75.469

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MHz, respectively, with a Bruker AM-300 spectrometer, operated at 297 K.

2.1. Preparation of adducts

Samples of the diol **1** and of the amine guest were separately dissolved in dichloromethane, acetonitrile, diethyl ether or petroleum, and the solutions mixed to give molar ratios of diol: amine ranging from 4:1 to 1:2. The solutions were set aside, and slow evaporation yielded crystals, either of an adduct, or of **1** admixed with crystals of the amine. In this manner the following were prepared:

Compound **2**: $(\mathbf{1})_2 \cdot$ HMTA (HMTA = hexamethylenetetramine). Anal. Found: C, 75.6; H, 6.1; N, 4.8. $C_{78}H_{72}Fe_2N_4O_4$ Calc.: C, 75.5; H, 5.9; N. 4.5% NMR ($CDCl_3$): δ_H 3.96 (m, 8H) and 4.16 (m, 8H) (4 × C_5H_4); 4.66 (s, 12H, 6 × CH_2); 4.70 (s, br, 4H, 4 × OH); 7.2–7.3 (m, 40H, 8 × C_6H_5); δ_c 68.2(d), 69.3(d) and 97.2(s) (C_5H_4); 74.4 (t, CH_2); 77.9 (s, C–OH); 126.7(d), 127.0(d), 127.3(d) and 147.3(s) (C_6H_5).

Compound **3**: **1** · TED (TED = 1,4-diazabicyclo-[2.2.2]octane). Anal. Found: C, 75.8; H, 6.0; N, 4.4. $C_{42}H_{42}FeN_2O_2$ Calc.: C, 76.1; H, 6.3; N, 4.2%. NMR ($CDCl_3$); δ_H 2.77 (s, 12H, 6 × CH_2); 3.96 (m, 4H) and 4.18 (m, 4H) (2 × C_5H_4);5.10 (s, br, 2H, 2 × OH); 7.1–7.3 (m, 20H, 4 × C_6H_5); δ_c 47.0 (t, CH_2); 68.2(d), 69.3(d) and 97.3(s) (C_5H_4); 77.9 (s,C–OH); 126.6(d), 127.0(d), 127.3(d) and 147.5(s) C_6H_5.

Compound **4**: **1** · (1,4-dimethylpiperazine). Anal. Found: C, 75.6; H 6.7; N, 4.3. $C_{42}H_{44}FeN_2O_2$ Calc.: C, 75.9; H, 6.7; N, 4.2%. NMR ($CDCl_3$): δ_H 2.27 (s, 6H, 2 × CH_3); 2.46 (m, br, 8H, 4 × CH_2); 3.94 (m, 4H) and 4.17 (m, 4H) (2 × C_5H_4); 4.35 (s, br, 2H, 2 × OH); 7.2–7.3 (m, 20H, 4 × C_6H_5); δ_c 46.0 (q, CH_3); 55.1 (t, CH_2); 68.4(d), 69.4(d) and 97.3(s) (C_5H_4); 78.1 (s, C–OH); 126.7(d), 126.9(d), 127.4(d) and 147.3(s) (C_6H_5).

Compound **5**: **1** · 2(3-pyridylferrocene). Anal. Found: C, 73.4; H, 5.3; N, 2.4. $C_{66}H_{56}Fe_3N_2O_2$ Calc.: C, 73.6; H, 5.2; N, 2.6% NMR ($CDCl_3$): δ_H ($CDCl_3$) 3.93 (m, 4H) and 4.18 (m, 4H) (2 × C_5H_4 in **1**); 4.03 (s, 10H, 2 × C_5H_4); 4.36 (m, 4H) and 4.68 (m, 4H) (2 × C_5H_4 in 3-pyridylferrocene); 4.95 (s, br, 2H, 2 × OH); 7.1–7.2 (m, 2H), 7.7 (m, 2H), 8.4 (m, 2H) and 8.7 (m, 2H) (2 × C_5H_4N); 7.2–7.3 (m, 20H, 4 × C_6H_5); δ_c 66.4(d), 69.5(d) and 81.5(s) (C_5H_4 in 3-pyridylferrocene); 68.2(d), 69.3(d) and 97.4(s) (C_5H_4 in **1**); 69.6 (d, C_5H_5); 78.0 (s, C–OH); 123.3(d), 133.0(d), 135.5(s), 146.6(d) and 147.1(d) (C_5H_4N); 126.7(d), 127.2(d), 127.3(d) and 147.6(s) (C_6H_5).

2.2. X-ray crystallography

Crystals of compound **2** suitable for X-ray examination were selected directly from the prepared sample. Attempts to grow suitable crystals of **3** have been unsuccessful: from solutions in most solvents, **3** was obtained as tight bundles of extremely thin fibres, but crystallisation from dichloromethane resulted in spontaneous phase-separation, providing a mixture, readily separable by hand, of orange crystals of **1** and colourless crystals of TED.

2.2.1. Crystal data for 2

$C_{78}H_{72}Fe_2N_4O_4 \cdot 0.42(H_2O)$, $M_r = 1248.66$, monoclinic, $a = 13.448(3)$ Å, $b = 22.340(3)$ Å, $c = 21.891(2)$ Å, $\beta = 105.38(1)°$, $U = 6341.4(16)$ Å^3, $Z = 4$, $D_c = 1.307$ g cm^{-3}, μ(Mo–K$_\alpha$) = 0.51 cm^{-1}, $\lambda = 0.71069$ Å, $F(000) = 2608$ (for $C_{78}H_{72}Fe_2N_4O_4$), space group $P2_1/n$ (No. 14) (from systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$).

2.3. Data collection

Cell dimensions were determined by least-squares refinement using the setting angles for 25 reflections in the range $10 \leq \theta \leq 20.5°$. Intensity data were measured at 20°C using a CAD4 diffractometer with graphite-monochromated Mo–K$_\alpha$, radiation. A total of 14367 reflections were measured, of which 13793 were unique, and 6405 had $I \geq 2\sigma(I)$. Lorentz and polarisation corrections were applied, together with a numerical absorption correction: maximum and minimum transmission coefficients were 0.889 and 0.817.

2.4. Structure solution and refinement

The structure was solved using the Patterson heavy-atom method, which revealed the position of the iron atom, followed by difference Fourier syntheses. Hydrogen atoms, which were all visible in difference maps, were included in the refinement in geometrically idealised positions, but restrained to ride on the carbon or oxygen atom to which they were bonded (C–H 0.95 Å; O–H 0.82 Å). Final refinement was by full-matrix least-squares calculations on F^2, using SHELXL-93 [8], initially with isotropic and subsequently with anisotropic thermal parameters for all non-hydrogen atoms. Examination of the refined structure using PLATON [9] revealed a single cavity per asymmetric unit of ca. 55 Å^3 volume; the three highest peaks in the penultimate difference map, diffuse peaks each corresponding to ca. 0.4 e Å^{-3}, were clustered around the centre of this cavity. The crystals of **2** were grown from acetonitrile, but there is no evidence for a linear three-atom fragment in the cavity: consequently the difference peaks were assigned to water molecules, and in the final cycles of refinement they were allowed for (at the fixed coordinates obtained from the difference

Table 1
Final fractional coordinates and equivalent isotropic thermal parameters

	x	y	z	U_{iso} (Å^2)
Diol A				
FeA	0.86334(3)	0.87585(2)	0.73103(2)	0.03901(12)
O1A	0.7394(2)	0.99137(9)	0.79192(11)	0.0542(6)
O2A	0.7577(2)	0.87859(8)	0.85472(9)	0.0453(5)
C1A	0.8054(2)	1.01351(13)	0.75519(14)	0.0432(7)
C11A	0.8820(2)	0.96562(12)	0.74876(14)	0.0400(7)
C12A	0.9141(2)	0.95005(13)	0.6935(2)	0.0502(8)
C13A	0.9942(2)	0.90749(14)	0.7118(2)	0.0545(9)
C14A	1.0115(2)	0.89613(13)	0.7765(2)	0.0509(8)
C15A	0.9438(2)	0.93228(12)	0.79961(15)	0.0414(7)
C2A	0.7782(2)	0.81763(12)	0.84084(13)	0.0375(7)
C21A	0.7817(2)	0.81917(12)	0.77224(13)	0.0354(7)
C22A	0.7139(2)	0.85244(13)	0.72394(14)	0.0443(8)
C23A	0.7385(2)	0.84169(15)	0.66599(14)	0.0525(9)
C24A	0.8204(2)	0.80035(14)	0.67764(14)	0.0503(8)
C25A	0.8470(2)	0.78597(12)	0.74272(14)	0.0417(7)
C31A	0.8620(2)	1.06746(12)	0.79111(14)	0.0411(7)
C32A	0.9670(2)	1.07697(14)	0.80195(15)	0.0492(8)
C33A	1.0136(3)	1.1261(2)	0.8355(2)	0.0580(9)
C34A	0.9570(3)	1.1673(2)	0.8586(2)	0.0660(10)
C35A	0.8524(3)	1.1589(2)	0.8475(2)	0.0705(11)
C36A	0.8049(3)	1.10949(14)	0.8145(2)	0.0586(9)
C41A	0.7391(2)	1.03249(14)	0.6897(2)	0.0489(8)
C42A	0.7755(3)	1.0724(2)	0.6530(2)	0.0674(10)
C43A	0.7191(4)	1.0866(2)	0.5921(2)	0.0926(14)
C44A	0.6242(4)	1.0614(2)	0.5675(2)	0.105(2)
C45A	0.5861(3)	1.0225(2)	0.6039(2)	0.0938(15)
C46A	0.6425(3)	1.0082(2)	0.6650(2)	0.0676(10)
C51A	0.6894(2)	0.77796(12)	0.84933(13)	0.0372(7)
C52A	0.6723(2)	0.77426(15)	0.90871(14)	0.0539(9)
C53A	0.5944(3)	0.7386(2)	0.9197(2)	0.0606(9)
C54A	0.5331(2)	0.70623(14)	0.8711(2)	0.0562(9)
C55A	0.5487(3)	0.7096(2)	0.8121(2)	0.0625(10)
C56A	0.6271(2)	0.74522(14)	0.80147(15)	0.0520(8)
C61A	0.8802(2)	0.79509(13)	0.88485(13)	0.0392(7)
C62A	0.9488(2)	0.8325(2)	0.92483(15)	0.0566(9)
C63A	1.0403(3)	0.8106(2)	0.9636(2)	0.0740(11)
C64A	1.0645(3)	0.7510(2)	0.9623(2)	0.0755(12)
C65A	0.9973(3)	0.7128(2)	0.9229(2)	0.0628(10)
C66A	0.9045(2)	0.73456(14)	0.88490(14)	0.0478(8)
Diol B				
FeB	0.60785(3)	0.83542(2)	1.24641(2)	0.03953(12)
O1B	0.7075(2)	0.82982(9)	1.11729(10)	0.0558(6)
O2B	0.7573(2)	0.94188(9)	1.19911(10)	0.0507(6)
C1B	0.6894(2)	0.77099(13)	1.13800(13)	0.0407(7)
C11B	0.6831(2)	0.77332(12)	1.20600(13)	0.0372(7)
C12B	0.6103(2)	0.74524(12)	1.23332(14)	0.0408(7)
C13B	0.6367(2)	0.75898(13)	1.29861(14)	0.0465(8)
C14B	0.7245(2)	0.79530(14)	1.31279(14)	0.0485(8)
C15B	0.7538(2)	0.80413(13)	1.25600(14)	0.0441(8)
C2B	0.6961(2)	0.96857(12)	1.23655(14)	0.0401(7)
C21B	0.6070(2)	0.92667(12)	1.23663(14)	0.0383(7)
C22B	0.5432(2)	0.89976(13)	1.18140(15)	0.0434(7)
C23B	0.4656(2)	0.86630(14)	1.1985(2)	0.0530(9)
C24B	0.4801(2)	0.87291(14)	1.2640(2)	0.0561(9)
C25B	0.5665(2)	0.90998(13)	1.28773(15)	0.0473(8)
C31B	0.7795(2)	0.73257(13)	1.13046(13)	0.0409(7)
C32B	0.8374(3)	0.69631(15)	1.1770(2)	0.0584(9)
C33B	0.9167(3)	0.6620(2)	1.1656(2)	0.0726(11)
C34B	0.9382(3)	0.6627(2)	1.1081(2)	0.0676(10)
C35B	0.8809(3)	0.6982(2)	1.0619(2)	0.0687(11)
C36B	0.8025(2)	0.7332(2)	1.07259(15)	0.0585(9)
C41B	0.5882(2)	0.7469(2)	1.09476(14)	0.0474(8)
C42B	0.5712(3)	0.6859(2)	1.0874(2)	0.0612(10)
C43B	0.4787(3)	0.6638(2)	1.0490(2)	0.0857(13)
C44B	0.4050(3)	0.7017(3)	1.0178(2)	0.097(2)
C45B	0.4191(3)	0.7615(3)	1.0239(2)	0.096(2)
C46B	0.5110(3)	0.7848(2)	1.0623(2)	0.0719(11)
C51B	0.6563(2)	1.02992(12)	1.20923(13)	0.0402(7)
C52B	0.7280(2)	1.07084(13)	1.19907(14)	0.0493(8)
C53B	0.6976(3)	1.12665(14)	1.1743(2)	0.0596(9)
C54B	0.5954(3)	1.1427(2)	1.1597(2)	0.0661(10)
C55B	0.5245(3)	1.1032(2)	1.1707(2)	0.0632(10)
C56B	0.5535(2)	1.04662(13)	1.19523(14)	0.0494(8)
C61B	0.7638(2)	0.97709(14)	1.3038(2)	0.0508(8)
C62B	0.8576(3)	0.9494(2)	1.3256(2)	0.0680(10)
C63B	0.9140(3)	0.9570(2)	1.3880(2)	0.106(2)
C64B	0.8783(5)	0.9932(3)	1.4282(3)	0.134(2)
C65B	0.7868(4)	1.0215(2)	1.4071(2)	0.113(2)
C66B	0.7308(3)	1.0141(2)	1.3453(2)	0.0748(11)
HMT				
N1	0.7527(2)	0.94726(11)	0.96419(12)	0.0547(7)
N2	0.7460(2)	0.97992(13)	1.06978(12)	0.0596(8)
N3	0.6459(2)	1.03292(15)	0.97628(14)	0.0706(9)
N4	0.8342(2)	1.04110(13)	1.00720(15)	0.0695(8)
C5	0.7536(3)	0.9292(2)	1.0287(2)	0.0658(10)
C6	0.8324(3)	1.0200(2)	1.0704(2)	0.0733(11)
C7	0.7354(4)	1.0711(2)	0.9803(2)	0.0860(13)
C8	0.8384(3)	0.9888(2)	0.9680(2)	0.0663(10)
C9	0.6504(3)	1.0123(2)	1.0401(2)	0.0695(11)
C10	0.6566(3)	0.9810(2)	0.9380(2)	0.0705(11)

Water [a]	x	y	z	U_{iso}	G.O.F.
O1	0.1959	0.5875	0.9910	0.483(75)	0.23(5) [a]
O2	0.1818	0.5932	0.9709	0.332(18)	0.06(3) [a]
O3	0.2753	0.5364	1.0190	0.372(60)	0.13(2) [a]

[a] The coordinates for the partial occupancy water molecules located between hydrogen bonded Diol–HMT–Diol units (atoms O1–O3) were obtained from the penultimate difference map. They were included in the final refinement round of calculations and their occupancies and isotropic thermal parameters allowed to refine.

map), and their occupancies and isotropic thermal parameters were allowed to refine. A final difference map was devoid of any significant features. The final residuals were $R(F)$, 0.0482; $wR(F^2)$, 0.0930, both calculated for all observed data.

All calculations were performed on a Silicon Graphics 4D-35TG workstation using SHELXL-93 [8] and NRCVAX [10]. The figures were prepared with the aid of ORTEP-II [11]. Final refined atom coordinates are given in Table 1, selected geometrical parameters are given in Table 2. A view of the hydrogen-bonded aggregate in compound **2** is given in Fig. 1, which also shows the atom-labelling scheme. Tables of H-atom coordinates and thermal parameters, and full lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Hydrogen-bonded adducts of 1

We previously reported [2] that the ferrocenediol **1** forms a 1 : 1 adduct with piperazine: the structure consists of infinite helical chains of alternating diol and piperazine molecules, in which there are only O–H ··· N hydrogen bonds; the N–H bonds of the piperazine guest do not take part in hydrogen bonding. We therefore reasoned that cyclic (and acyclic) tertiary amines should also form similar adducts and hence, provided that O–H ··· N hydrogen bonds were the only type formed, appropriate selection of a poly-aza guest could, in principle, provide hydrogen-bonded arrays which were one-, two-, or three-dimensional.

With hexamethylenetetramine, $[(CH_2)_6N_4]$ HMTA, as the guest, crystallisation of mixtures of widely different stoichiometries gave only a single crystalline product, the 2 : 1 adduct **2** $[Fe(C_5H_4CPh_2OH)_2]_2 \cdot$ HMTA. In this adduct, there is a perfect matching of the numbers of O–H hydrogen-bond donors and the number of nitrogen atoms (potential hydrogen-bond acceptors), and we therefore expected the formation of an extended three-dimensional network containing only O–H ··· N hydrogen bonds.

The structure, determined by X-ray analysis and described below, in fact contains a finite hydrogen-bonded aggregate comprising two molecules of the diol **1** and one of HMTA and containing both intramolecular O–H ··· O and intermolecular O–H ··· N hydrogen bonds; two of the four nitrogen atom acceptors take no part in the hydrogen bonding. In this respect, adduct **2** shows some similarity to the 1 : 1 adduct formed by the diol **1** with 4,4′-bipyridyl [2]; in that adduct, the structure contains a hydrogen-bonded aggregate of two molecules of **1** and one molecule of the bipyridyl containing two intramolecular O–H ··· O and two intermolecular O–H ··· N hydrogen bonds, together with a second molecule of the bipyridyl lying in a cavity in the structure but not participating in hydrogen bonds. Thus in the adducts formed between the diol **1** and both 4,4′-bipyridyl or HMTA, one-half of the nitrogen atoms present are not involved in intermolecular hydrogen bonding.

The chain-type structure found [2] for the 1 : 1 adduct formed between the diol **1** and piperazine provides the most plausible structural model for adducts **3** and **4**, formed respectively from TED and 1,4-dimethylpiperazine. However the observation that even with non-aromatic tertiary amines (such as HMTA), some nitrogen acceptors of hydrogen bonds may be unused

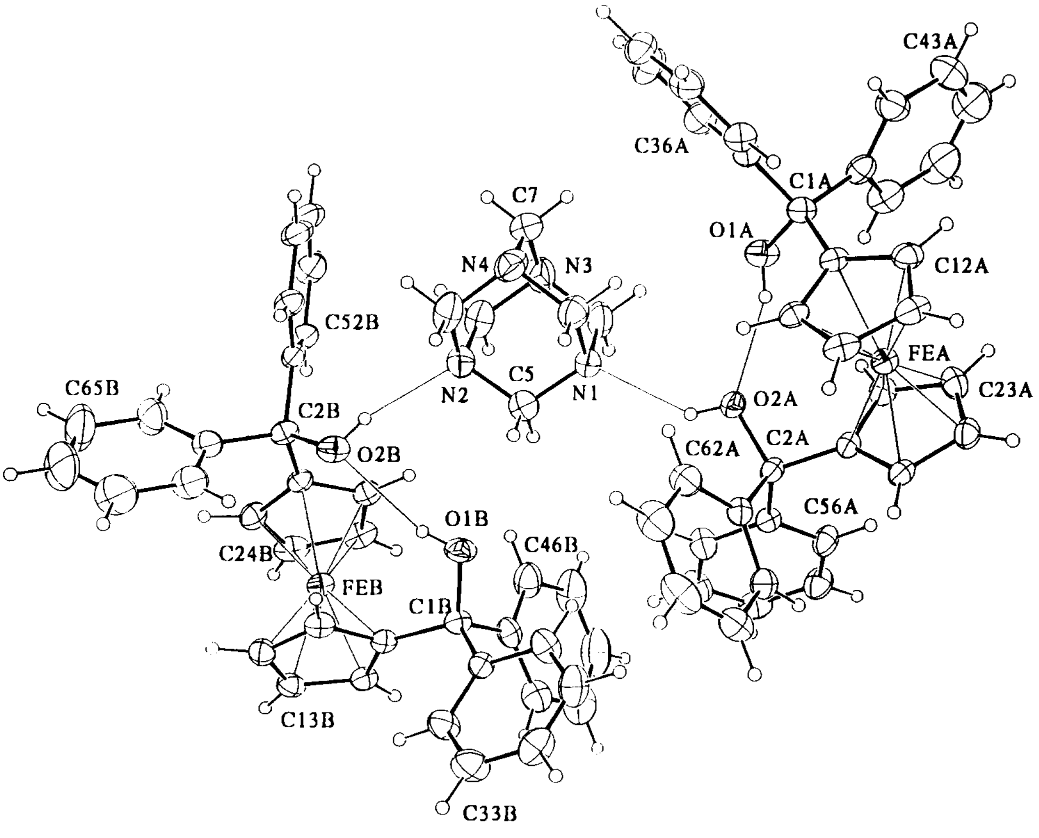

Fig. 1. View of the hydrogen-bonded aggregate in the adduct 2, showing the atom-labelling scheme. The non-hydrogen atoms are depicted with their thermal ellipsoids at the 35% level; for clarity, hydrogen atoms are shown as small spheres of arbitrary size.

Table 2
Selected dimensions (distances in Å, angles in °) for **2**

Bond lengths in diol components	Diol A	Diol B
C(11)–C(12)	1.430(4)	1.421(4)
C(12)–C(13)	1.413(4)	1.412(4)
C(13)–C(14)	1.395(4)	1.398(4)
C(14)–C(15)	1.408(4)	1.414(4)
C(15)–C(11)	1.412(4)	1.423(4)
Fe–Cp1	1.649	1.649
C(21)–C(22)	1.411(4)	1.418(4)
C(22)–C(23)	1.414(4)	1.412(4)
C(23)–C(24)	1.408(4)	1.403(4)
C(24)–C(25)	1.411(4)	1.409(4)
C(25)–C(21)	1.428(4)	1.418(4)
Fe–Cp2	1.650	1.654
C(1)–C(11)	1.518(4)	1.514(4)
C(1)–O(1)	1.435(3)	1.432(3)
C(1)–C(31)	1.528(4)	1.530(4)
C(1)–C(41)	1.534(4)	1.534(4)
C(2)–C(21)	1.516(4)	1.521(4)
C(2)–O(2)	1.438(3)	1.436(3)
C(2)–C(51)	1.537(4)	1.534(4)
C(2)–C(61)	1.538(4)	1.524(4)
Torsional angles in diol components		
C(1n)–Cp1–Cp2–C(2n) (mean value)	−77.5	−80.9
O(1)–C(1)–C(11)–C(12)	137.7(3)	135.1(3)
C(31)–C(1)–C(11)–C(12)	−105.2(3)	−107.3(3)
C(41)–C(1)–C(11)–C(12)	17.1(4)	15.1(4)
O(2)–C(2)–C(21)–C(22)	−40.8(3)	−47.6(3)
C(51)–C(2)–C(21)–C(22)	76.3(3)	73.3(3)
C(61)–C(2)–C(21)–C(22)	−161.4(3)	−166.2(3)

Hydrogen-bond distances and angles

O(1A) ··· O(2A)	2.849(3)	O(2A) ··· N(1)	2.861(3)
O(1B) ··· O(2B)	3.047(3)	O(2B) ··· N(2)	2.921(3)
O(1A)–H(1A) ··· O(2A)	154.9	O(2A)–H(2A) ··· N(1)	141.8
O(1B)–H(1B) ··· O(2B)	153.5	O(2B)–H(2B) ··· N(2)	161.5

Bond lengths in HMTA component

N(1)–C(5)	1.465(4)	N(1)–C(8)	1.465(4)	N(1)–C(10)	1.474(1)
N(2)–C(5)	1.468(4)	N(2)–C(6)	1.464(4)	N(2)–C(9)	1.468(4)
N(3)–C(7)	1.459(5)	N(3)–C(9)	1.458(4)	N(3)–C(10)	1.461(4)
N(4)–C(6)	1.467(4)	N(4)–C(7)	1.464(5)	N(4)–C(8)	1.459(4)

and intramolecular O–H ··· O hydrogen bonds are preferred, opens up the alternative possibility that the structural motif in each of **3** and **4** may be a finite aggregate, comprising in each case one molecule of diol and one molecule of amine. In such an aggregate, one O–H ··· O and one O–H ··· N hydrogen bond would accommodate both hydroxyl hydrogens, leaving one half of the nitrogen atoms uninvolved in hydrogen bonding. IR spectra are, unfortunately, inconclusive on the hydrogen bonding present in **3** and **4**, and a definitive assignment of their structures cannot be made in the absence of X-ray diffraction data. It may, however, be noted that the 1:2 adduct of diol **1** with 1,4-dioxan is isostructural [2] with the 1:2 pyridine adduct [1], so that in this dioxan adduct one half of the dioxan oxygen atoms are not involved in hydrogen bonding. In view of the ease of adduct formation with the secondary amine piperazine (1,4-diazacyclohexane) it is surprising that no adduct formation was found either with 1,4,7-triazacyclononane or with 1,4,8,11-tetraazacyclotetradecane. Similarly, given the ease of adduct formation with HMTA and TED, it is surprising that no adduct was formed by the simple acyclic analogue bis(dimethylamine)methane.

In the 1:2 pyridine adduct [1], one molecule of pyridine is hydrogen bonded to each hydroxyl group of the diol, although the hydroxyl atoms are disordered, and possibly mobile. This structure provides the most plausible model for the 1:2 adduct **5** formed by **1** and 3-pyridylferrocene: the alternative structure consists of a 1:1 hydrogen-bonded aggregate containing ordered O–H ··· O and O–H ··· N hydrogen bonds with the second molecule of 3-pyridylferrocene free in the structure. No adducts were formed between the diol **1** and any of 2- or 4-nitrophenylferrocene, 2-or 4-aminophenylferrocene or 1,1′-bis(2-nitrophenyl)ferrocene, nor was any adduct formed between 4-aminophenylferrocene and either 2- or 4-nitrophenylferrocene. This last observation is in marked contrast to the normal behaviour of organic systems containing both nitro and amino groups: nitroanilines, for example, normally form strongly hydrogen-bonded systems, with both oxygens of the nitro group acting as acceptor from a single N–H bond [12].

3.2. Crystal and molecular structure of adduct 2

The adduct **2**, $[Fe(C_5H_4CPh_2OH)_2]_2 \cdot HMTA$ crystallises in the monoclinic space group $P2_1/n$ with two molecules of the diol (labelled **A** and **B**) and one of HMTA in the asymmetric unit. There is therefore no crystallographic symmetry imposed upon either component in **2**. The structure (Fig. 1) consists of a finite aggregate in which each molecule of the diol contains an intramolecular O–H ··· O hydrogen bond, and in which each diol molecule forms one O–H ··· N hydrogen bond to the HMTA component, leaving two of the four nitrogen atoms free of hydrogen bonds. The O ··· O distances are 2.849(3) Å in diol **A** and 3.047(3) Å in diol **B**, and the corresponding O ··· N distances O2A ··· N1 and O2B ··· N2 are 2.861(3) Å and 2.921(3) Å. The O ··· O and O ··· N distances in the similar adducts of **1** with pyridine [1] and with 4,4′-bipyridyl [2] are 2.824(3) Å and 2.948(2) Å (O ··· O) and 2.932(4) Å and 2.799(2) Å (O ··· N). In all three of these adducts, the hydrogen-bonding motif has graph set **S(8)D** [13,14].

Within the ferrocenediol units, the C–C distances (Table 2) in the cyclopentadienyl rings range from 1.395(4) Å to 1.430(4) Å with a mean value of 1.413 Å and the mean C–O distance is 1.435 Å: these values are typical of those found in other adducts of the diol **1**. The mean value of the torsion angle C(1*n*)–Cp1–

Cp2–C(2*n*) (for $n = 1$–5), where Cp1 and Cp2 represent the centroids of the C_5 rings, is −77.5° for diol **A** and −80.9° for diol **B**: because for perfect eclipsing of these rings, the mean value should be $(72 \times n)°$ (n = integer or zero), the observed values indicate nearly eclipsed rings with the exocyclic C–C bonds offset by one-fifth of a turn. The interplane angles between the C_5 rings are 1.9(2)° for diol **A** and 2.4(2)° for diol **B**.

The conformation about the exocyclic C–C bonds (Table 2) is virtually identical, for both diol components, to that of the diol component in the adduct of **1** with 4,4′-bipyridyl [2]. Each diol component **A** and **B** has approximate two-fold rotational symmetry, although there is no crystallographically imposed symmetry.

In the HMTA fragment the mean values of the C–N distance 1.464 Å and the C–N–C and N–C–N angles, 107.5° and 113.2° are identical with (librationally uncorrected) values measured at 298 K for free HMTA [15]; the slight difference in the mean C–N distances associated with the hydrogen-bonded nitrogen, 1.467 Å, and the free nitrogen, 1.461 Å is probably not significant.

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