Hydrogen-bonded Adducts of Ferrocene-1,1′-diylbis(diphenylmethanol): Crystal and Molecular Structures of Adducts with Methanol (1 : 1) and Pyridine (1 : 2)†

George Ferguson,[a] John F. Gallagher,[a] Christopher Glidewell*[,b] and Choudhury M. Zakaria[b]

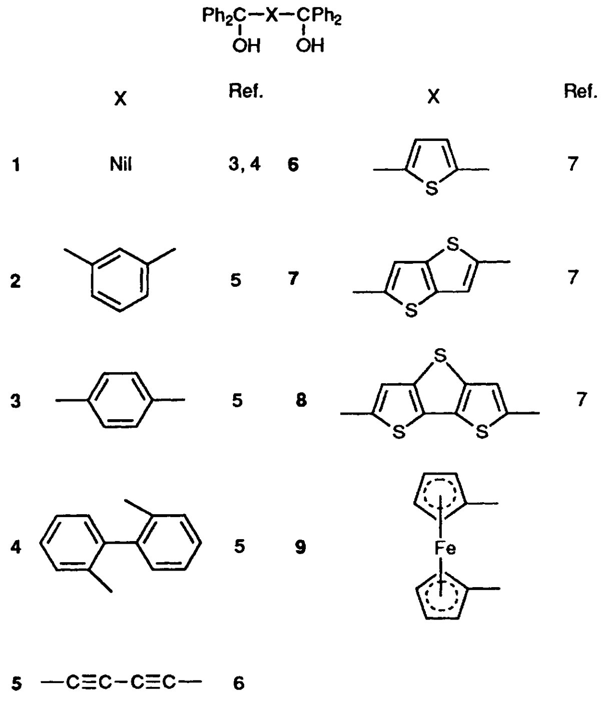
[a] *Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada*

[b] *School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK*

Ferrocene-1,1′-diylbis(diphenylmethanol), $[Fe(C_5H_4CPh_2OH)_2]$, forms hydrogen-bonded host–guest adducts with a wide range of hydrogen-bond donors and acceptors. Adducts with a diol:guest ratio of 1:1 were formed by MeOH, EtOH, Me_2SO, Me_2NCHO, piperazine, and 4,4′-bipyridyl and 1:2 adducts by Me_2SO, dioxane, pyridine and piperidine. The 1:1 adduct with MeOH has been shown to be triclinic, space group $P\bar{1}$ with a = 8.7624(3), b = 12.2797(6), c = 14.8773(8) Å, α = 106.572(4), β = 97.879(4), γ = 100.873(4)° with a final R of 0.044 for 4982 observed reflections. The structure consists of a centrosymmetric assembly of two molecules of the host diol and two molecules of the guest MeOH, hydrogen bonded together to form a chair conformation $(OH)_6$ ring. The 1:2 adduct with pyridine has been shown to be monoclinic, space group $C2/c$ with a = 16.6252(10), b = 11.1016(9), c = 20.9440(16) Å, β = 107.855(6)° with a final R of 0.042 for 3260 observed reflections. In the structure the diol lies on a two-fold rotation axis with its hydroxyl hydrogens disordered and participating in both intramolecular O–H⋯O and intermolecular O–H⋯N hydrogen bonding with the two pyridine guest molecules.

Triphenylmethanol, which crystallises as tetrahedral tetramers,[1] forms inclusion compounds with a wide range of hydrogen-bond acceptors.[2] It thus acts as the prototype for a range of related host molecules **1**–**9**, each containing two $Ph_2C(OH)$ fragments.[3–7]

We have now characterised the ferrocene derivative **9**, ferrocene-1,1′-diylbis(diphenylmethanol) and report upon its inclusion compounds formed with a wide range of hydrogen-bond acceptors. We have also synthesised several other ferrocenediols, **10**–**12**, which are analogues of **9** although not containing $Ph_2C(OH)$ groups, and report some preliminary studies on these.



Experimental

Diethyl ether and light petroleum (b.p. 40–60 °C) were dried by reflux over sodium diphenylketyl, dichloromethane by reflux over calcium hydride. Elemental analysis was by the Microanalytical Laboratory of this Department. Proton and ^{13}C NMR spectra were recorded at 300.133 and 75.469 MHz respectively using a Bruker AM-300 spectrometer at 294 K.

*Preparations.—Ferrocene-*1,1′*-diylbis(diphenylmethanol)* **9**. Phenyllithium (6.1 cm^3 of a solution in hexane; 1.8 mol dm^{-3}, 11.0 mmol) was added under nitrogen and with stirring to a solution of 1,1′-dibenzoylferrocene (2.75 g, 5.5 mol) in diethyl ether (50 cm^3). The mixture was stirred at room temperature for 15 h, then hydrolysed with an excess of dilute sulfuric acid, before extraction with diethyl ether (2 × 50 cm^3). The ether extracts were combined, washed with water and dried over Na_2SO_4 before removal of the solvent. Recrystallisation from dichloromethane–light petroleum gave compound **9** as deep orange crystals in 86% yield, m.p. 186 °C (Found: C, 78.5; H, 5.3. $C_{36}H_{30}FeO_2$ requires C, 78.6; H, 5.5%). NMR ($CDCl_3$): δ_H 3.94 (m, 4 H) and 4.16 (m, 4 H) (2 C_5H_4), 4.40 (s, br, 2 H, 2 OH) and 7.1–7.3 (m, 20 H, 4 C_6H_5); δ_C 68.3 (d), 69.3 (d) and 97.2 (s) (C_5H_4), 78.1 (s, COH), 126.7 (d), 127.0 (d), 127.5 (d) and 147.2 (s) (C_6H_5).

Adducts of compound **9**. For guests which are liquid at room temperature, samples of compound **9** were dissolved in an excess of the guest and crystals were grown by slow evaporation of the resulting solutions. The crystals were filtered off and dried

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

over calcium chloride. In this manner the following were prepared.

Compound **9a** : **9**•MeOH (Found: C, 76.3; H, 6.1. $C_{37}H_{34}FeO_3$ requires C, 76.3; H, 6.1%). Composition confirmed by X-ray structure analysis.

Compound **9b**:**9**•EtOH (Found: C, 76.9; H, 5.7. $C_{38}H_{36}FeO_3$ requires C, 76.5; H, 6.1%). NMR ($CDCl_3$): δ_H 1.24 (t, J = 7, 3 H, CH_3), 1.62 (s, br, 1 H, CH_2OH), 3.71 (q, J = 7 Hz, 2 H, CH_2), 3.94 (m, 4 H) and 4.16 (m, 4 H) (2 C_5H_4), 4.13 (s, 2 H, 2 OH) and 7.1–7.3 (m, 20 H, 4 C_6H_5); δ_C 18.4 (q, CH_3), 58.5 (t, CH_2), 68.3 (d), 69.3 (d) and 97.2 (s) (C_5H_4), 78.1 (s, COH), 126.7 (d), 127.0 (d), 127.4 (d) and 147.2 (s) (C_6H_5).

Compound **9c**:**9**•2Me$_2$SO. NMR ($CDCl_3$): δ_H 2.57 (s, 12 H, 4 CH_3), 3.93 (m, 4 H) and 4.18 (m, 4 H) (2 C_5H_4), 4.89 (s, br, 2 H, 2 OH) and 7.1–7.3 (m, 20 H, 4 C_6H_5); δ_C 40.8 (q, CH_3), 68.3 (d), 69.3 (d) and 97.2 (s) (C_5H_4), 78.1 (s, COH), 126.7 (d), 127.0 (d), 127.4 (d) and 147.2 (s) (C_6H_5).

Compound **9d**:**9**•2C_5H_5N (Found: C, 79.0; H, 6.0; N, 3.9. $C_{46}H_{40}FeN_2O_2$ requires C, 78.0; H, 5.7; N, 4.0%). NMR ($CDCl_3$): δ_H 3.95 (m, 4 H) and 4.18 (m, 4 H) (2 C_5H_4), 5.05 (s, br, 2 H, 2 OH); 7.1–7.3 (m, 20 H, 4 C_6H_5), 7.6–7.7 (m, 4 H) and 8.5–8.6 (m, 6 H) (2 C_5H_5N); δ_C 68.3 (d), 69.4 (d) and 97.4 (s) (C_5H_4), 78.1 (s, COH), 126.7 (d), 127.1 (d), 127.4 (d) and 147.5 (s) (C_6H_5), 123.7 (d), 136.0 (d) and 149.7 (d) (C_5H_5N).

Compound **9e**:**9**•2O(CH_2CH_2)$_2$O. NMR ($CDCl_3$): δ_H 3.69 (s, 16 H, 8 CH_2), 3.95 (s, br, 2 H, 2 OH); 4.10 (m, 4 H) and 4.33 (m, 4 H) (2 C_5H_4), and 7.1–7.3 (m, 20 H, 4 C_6H_5); δ_C 67.1 (t, CH_2), 69.9 (d), 70.8 (d) and 98.6 (s), (C_5H_4), 78.1 (s, COH), 126.9 (d), 127.0 (d), 127.5 (d) and 147.0 (s) (C_6H_5).

Compound **9f**:**9**•Me$_2$NCHO (Found: C, 75.0; H, 6.2; N, 2.6. $C_{39}H_{37}FeNO_3$ requires C, 75.1; H, 5.9: N, 2.2%). NMR ($CDCl_3$): δ_H 2.85 (s, 3 H, CH_3), 2.93 (s, 3 H, CH_3), 3.96 (m, 4 H) and 4.22 (m, 4 H) (2 C_5H_4), 4.34 (s, br, 2 H, 2 OH), 7.1–7.3 (m, 20 H, 4 C_6H_5) and 7.97 (s, 1 H, CHO); δ_C 31.4 (q) and 36.5 (q) (2 CH_3) 68.7 (d), 69.7 (d) and 97.6 (s) (C_5H_4) 78.2 (s, COH), 126.8 (d), 127.0 (d), 127.5 (d) and 147.3 (s) (C_6H_5) and 162.5 (s, C=O).

Compound **9g**:**9**•2HN(CH_2)$_5$ (Found: C, 75.7; H, 7.3; N, 3.8. $C_{46}H_{52}FeN_2O_2$ requires C, 76.7; H, 7.2; N, 3.9%). NMR ($CDCl_3$): δ_H 1.4–1.6 (m, 12 H, 6 CH_2), 2.6–2.8 [m, 8 H, 2 N(CH_2)$_2$], 3.92 (m, 4 H) and 4.24 (m, 4 H) (2 C_5H_4) and 7.1–7.3 (m, 20 H, 4 C_6H_5); δ_C 24.9 (t), 27.0 (t) and 47.1 (t) [HN(CH_2)$_5$] 68.2 (d), 69.4 (d), and 97.4 (s) (C_5H_4), 78.0 (s, COH), 126.7 (d), 127.2 (d), 127.4 (d) and 147.7 (s) (C_6H_5).

No adducts were found with CH_2Cl_2, MeCN or Me$_2$CO.

For guests which are solid at room temperature, equimolar quantities of compound **9** and the guest were separately dissolved in CH_2Cl_2 and the solutions were then mixed: slow evaporation yielded crystals, either of **9** or of the adduct. In this manner the following were prepared.

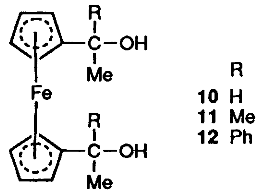
Compound **9h**:**9**•4,4′-bipy (bipy = bipyridyl) (Found: C, 78.1; H, 5.1; N, 4.0. $C_{46}H_{38}FeN_2O_2$ requires C, 78.2; H, 5.4; N, 4.0%). NMR ($CDCl_3$): δ_H 3.94 (m, 4 H) and 4.16 (m, 4 H) (2 C_5H_4), 4.90 (s, br, 2 H, 2 OH), 7.1–7.3 (m, 20 H, 4 C_6H_5), 7.4–7.6 (m, 4 H) and 8.5–8.8 (m, 4 H) (C_5H_4N); δ_C 68.4 (d), 69.4 (d) and 97.2 (s) (C_5H_4), 78.0 (s, COH), 126.8 (d), 127.1 (d), 127.4 (d) and 147.5 (s) (C_6H_5), 121.4 (d), 145.5 (d) and 150.6 (s) (C_5H_4N).

Compound **9i**:**9**•pipz (pipz = piperazine) (Found: C, 75.4, H, 6.6; N, 4.4. $C_{40}H_{40}FeN_2O_2$ requires C, 75.5; H, 6.3; N, 4.4%). NMR ($CDCl_3$): δ_H 2.80 (s, 8 H, 4 CH_2), 3.94 (m, 4 H) and 4.16 (m, 4 H) (2 C_5H_4) and 7.1–7.3 (m, 20 H, 4 C_6H_5); δ_C 47.0 (t, CH_2), 68.3 (d), 69.4 (d) and 97.3 (s) (C_5H_4), 78.1 (s, COH), 126.8 (d), 127.1 (d), 127.4 (d) and 147.5 (s) (C_6H_5).

No adducts were formed between compound **9** and 4-cyanophenol, 4-amino-, 4-cyano- and 3-hydroxy-pyridine.

All adducts were deep orange and all melted at, or around, 186 °C, indicating irreversible decomposition to **9**, m.p. 186 °C.

Competition experiments were carried out by dissolving the diol **9** in an excess of an equimolar mixture of two liquid guests and isolating the crystals formed after slow evaporation. In general, either a single adduct as described above or a mixture of such adducts was isolated except for Me$_2$SO–MeOH mixtures which yielded **9j**, **9**•Me$_2$SO (Found: C, 71.1; H, 5.9. $C_{36}H_{30}FeO_3S$ requires C, 72.6; H, 5.8%). NMR ($CDCl_3$): δ_H 2.57 (s, 6 H, 2 CH_3), 3.94 (m, 4 H) and 4.19 (m, 4 H) (2 C_5H_4), 4.90 (s, br, 2 H, 2 OH) and 7.1–7.3 (m, 20 H, 4 C_6H_5).



R	
10	H
11	Me
12	Ph

1,1′-*(Ferrocene-*1,1′-*diyl)diethanol* **10**. The compound was prepared as a mixture of diastereoisomers by reduction of 1,1′-diacetylferrocene with $LiAlH_4$.[8] Repeated fractional crystallisation from hexane[8] gave a single isomer, m.p. 99–100 °C (lit.,[8] 99.5–100.5 °C) (Found: C, 62.0; H, 6.7. $C_{14}H_{18}FeO_2$ requires C, 61.3; H, 6.6%). NMR ($CDCl_3$): δ_H 1.52 (d, J = 6.3, 6 H, 2 CH_3), 1.71 (s, br, 2 H, 2 OH), 3.81 (q, J = 6.3 Hz, 2 H, 2 CH), 4.02 (m, 2 H), 4.14 (m, 2 H) and 4.25 (m, 4 H) (2 C_5H_4); δ_C 22.2 (q, CH_3), 65.1 (d), 68.2 (d), 70.1 (d), 71.2 (d) and 90.5 (s) (C_5H_4) and 72.1 (d, COH).

2,2′-*(Ferrocene-*1,1′-*diyl)dipropan-*2-*ol* **11**. Methyllithium (15.9 cm^3 of a solution in diethyl ether; 1.4 mol dm^{-3}, 22.2 mmol) was added under nitrogen to a solution of 1,1′-diacetylferrocene (2.00 g, 7.4 mmol) in diethyl ether (50 cm^3). The mixture was stirred at room temperature for 16 h, then quenched with dilute sulfuric acid. It was extracted with diethyl ether (2 × 50 cm^3) and the ether extract was washed with water before drying and subsequent removal of the solvent. The resulting deep yellow oil was recrystallised from hexane to give dark yellow crystals. Examination of this product by ^{13}C NMR spectroscopy revealed the presence of at least four ferrocenyl species: hand selection provided crystals of compound **11** suitable for X-ray structure analysis.[9] (Found: C, 63.7; H, 7.9. $C_{16}H_{22}FeO_2$ requires C, 63.6; H, 7.7%).

1,1′-*Diphenyl-*1,1′-*(ferrocene-*1,1′-*diyl)diethanol*, **12**. This compound was prepared from 1,1′-diacetylferrocene in a manner analogous to that for compound **9**. An NMR examination of the crude reaction product showed the presence of only a single diastereoisomer: recrystallisation from hexane provided **12**, m.p. 147–148 °C (Found: C, 73.5; H, 5.9. $C_{26}H_{26}FeO_2$ requires C, 73.2; H, 6.1%). NMR ($CDCl_3$): δ_H 1.90 (s, 6 H, 2 CH_3), 4.25 (m, 4 H) and 4.39 (m, 4 H) (2 C_5H_4), 4.30 (s, br, 2 H, 2 OH) and 7.1–7.5 (m, 10 H, 2 C_6H_5); δ_C 31.3 (q, CH_3), 66.9 (d), 67.6 (d), 67.7 (d), 68.0 (d) and 99.7 (s) (C_5H_4), 73.0 (s, COH), 124.8 (d), 126.5 (d), 127.9 (d) and 148.2 (s) (C_6H_5).

X-Ray Crystallography.—Crystals of adducts **9a** and **9d** were selected directly from the prepared samples. Details of the X-ray experimental conditions, cell data, data collection and refinement are summarised in Table 1. Adduct **9a** crystallised in the triclinic system, space groups $P\bar{1}$ or $P1$, the former was assumed and confirmed by successful analysis. The structure was solved by the heavy-atom method which revealed the non-hydrogen atoms and refined using the NRCVAX[10] suite of programs. Hydrogen atoms (visible in difference maps at an intermediate stage of the refinement) were included at geometrically idealised positions, but restrained to ride on the carbon atom to which they were bonded (C-H 0.95 Å); the O–H hydroxyl hydrogens were refined isotropically. Refinement was by full-matrix least-squares calculations on F, initially with isotropic and later with anisotropic thermal parameters for all non-hydrogen atoms.

The host-guest system **9d** crystallised in the monoclinic system and the space group was determined from the systematic absences (hkl absent if $h + k = 2n + 1$, $h0l$ absent if $l = 2n + 1$) which allows the space group to be either $C2/c$ or Cc; the former was assumed and confirmed by the analysis. Hydrogen atoms attached to carbon were included at geometrically idealised positions, but restrained to ride on the carbon atom to which they were bonded (C–H 0.95 Å); the hydroxyl hydrogens were disordered over two orientations and were included in the structure-factor calculations at the positions derived from the difference maps in the latter stages of refinement. Refinement was as for **9a**.

The figures were prepared with the aid of ORTEP II[11] and PLUTON.[12]

Refined atomic coordinates for non-hydrogen atoms are in Tables 2 and 3, and selected molecular dimensions in Tables 4 and 5. Fig. 1 shows the asymmetric unit for **9a** and Fig. 3 shows the host–guest arrangement for **9d**, each with the atom-numbering scheme. Figs 2 and 4 show stereoviews of **9a** and **9d**.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles. Copies of the structure factor listing are available from the authors.

Results and Discussion

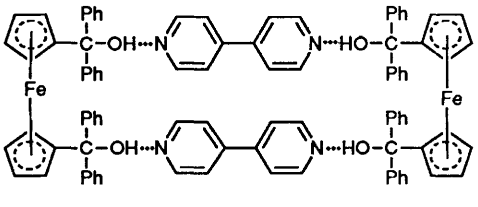
Ferrocenediols.—The diols **9** and **12** were readily formed by reaction of phenyllithium with 1,1′-dibenzoylferrocene or 1,1′-diacetylferrocene respectively, followed by acid work-up. In diol **12**, there are two stereogenic centres in the molecules, so that in principle both racemic (*RR* + *SS*) or *meso* (*RS* ≡ *SR*) forms are possible. Regardless of the stereochemistry *R* or *S* at each stereogenic centre, their presence renders each of the four CH carbons in the cyclopentadienyl rings non-isochronous: however the two-fold rotation axis in the racemic form and the mirror plane in the *meso* form mean that, for each form, the two rings are equivalent leading to only five cyclopentadienyl ^{13}C NMR resonances for each form. Examination of the crude reaction mixture from the preparation of **12** showed only a single diastereoisomer to be present. Subsequent X-ray analysis[13] demonstrates that **12** is racemic: the structure consists of hydrogen-bonded dimeric aggregates either of two *RR* or of two *SS* molecules, the two types of dimer being present in equal numbers and related by centres of inversion. Entirely similar dimeric aggregates are present in the structure of **9**,[14] and in both **9** and **12** the hydroxyl hydrogen atoms, in a hydrogen-bonding motif[15,16,*] $\mathbf{R}_4^4(8)$, appear disordered with 50% occupancy of two sites: ^{2}H NMR spectroscopy of polycrystalline solid **9** selectively deuteriated in the hydroxyl groups indicates[17] that the hydroxyl hydrogens are mobile in the solid state, jumping between the two sites identified in the X-ray analysis.

The diol **10** has been previously prepared[8] and separated by fractional crystallisation into two pure forms, m.p. 99.5–100.5 °C assigned[8] as the *meso* form and m.p. 86–86.5 °C assigned as the racemic form. The basis for these stereochemical assignments is not described in the original report.[8] We have repeated this work and have obtained the high-melting form using precisely the procedure described[8] and have shown[13] that this isomer is in fact the racemic form, which crystallises as centrosymmetric hydrogen-bonded dimers containing one *RR* and one *SS* molecule: the hydrogen-bonding motif is again $\mathbf{R}_4^4(8)$, but with fully ordered hydrogens. We have been unable to isolate the other, *meso* form free from either the racemic form or, more seriously, from the dehydration products, the two isomeric 7-oxa[3]ferrocenophanes. It is of some interest that attack upon 1,1′-diacetylferrocene by hydride ion (or masked hydride from AlH_4^-) provides both racemic and *meso* forms in comparable yields, while corresponding attack by phenyl anions yields only the racemic isomer: in this latter case the stereochemistry of attack at the first acyl group completely determines the stereochemistry of the subsequent reaction at the second acyl site, whereas with hydride the stereochemistry of the second addition is essentially independent of the first.

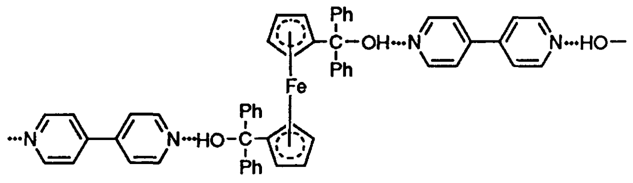
Although the diol **11** has been reported previously as a product from the addition of acetone to 1,1′-dilithioferrocene, we sought a preparation from 1,1′-diacetylferrocene. Use of methyllithium provided a complex mixture consistent with the very easy dehydration of this diol[18] to yield both vinylferrocenes and 7-oxa[3]ferrocenophanes. However, separation by hand of the crystalline product provided sufficient crystals of **11** for X-ray analysis, although clearly this is not a practical route to **11**.

Hydrogen-bonded Adducts of Ferrocenediols.—When crystallised from dichloromethane the diol **9** forms solvent-free crystals which contain no voids large enough to accommodate solvent molecules:[14] it should however be noted that dichloromethane can form hydrogen bonds to an appropriately oriented pair of phenyl groups by means of C–H ··· π(arene) interactions.[19] Based upon this observation dichloromethane provides a convenient solvent for formation of adducts between the diol **9** and solid guests.

Crystallisation of compound **9** from pyridine produces an adduct, characterised analytically and spectroscopically as having a host : guest ratio of 1 : 2, *i.e.* $\mathbf{9}\cdot2C_5H_5N$. Each pyridine is hydrogen bonded to one hydroxyl group of **9**: the structure has been determined by X-ray analysis, and the structure and the hydrogen bonding are described in detail below. With 4,4′-bipyridyl an adduct of 1 : 1 stoichiometry was obtained and shown by infrared spectroscopy to be a new compound rather than a microcrystalline mixture: the region 4000–2500 cm^{-1} for the adduct showed an absorption pattern different from that arising from summation of the two individual components. There are two plausible structures for this adduct, an isolated molecular aggregate **Ia** and a chain structure **Ib**. A distinction between these can only be made when single crystals suitable for X-ray diffraction become available. By contrast with pyridine and 4,4′-bipyridyl, no adducts were obtained with either acetonitrile or 4-cyanopyridine.



Ia



Ib

With Me$_2$SO a 1 : 2 adduct **9c** was formed when the diol **9** was crystallised from neat Me$_2$SO but when an equimolar mixture of Me$_2$SO and methanol was used a 1 : 1 adduct **9j** was obtained: **9c** was readily converted into **9j** by standing in air for some days. By analogy with the pyridine adduct of **9**, and the 1 : 2 adduct formed by diol **1** with Me$_2$SO, the most plausible structure for **9c** has a Me$_2$SO molecule hydrogen bonded to each hydroxyl group of the diol. A similar arrangement was found for the 1 : 2 adduct formed between the fluorenyl analogue of diol **7** and

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[*] Hydrogen-bonded motifs and networks can be described and codified using pattern designators[15,16] of the general type $\mathbf{G}_d^a(r)$. The descriptor **G** may be **C** (chain), **D** (dimer or other finite set), **R** (ring) or **S** (self) (*i.e.* an intramolecular hydrogen bond). The degree *r* represents the total number of atoms in a ring, or in the repeating unit of a chain, the superscript *a* indicates the number of hydrogen-bond acceptors in the pattern **G** and the subscript *d* indicates the number of hydrogen-bond donors.

Me_2SO.[7] By contrast with these diols, it has been found that diols **4**,[5] **6**[7] and **8**[7] all form 1 : 1 adducts with Me_2SO providing structural models for **9j**, while Ph_3COH forms a 2 : 1 adduct in which both oxygen lone pairs of the Me_2SO act as hydrogen-bond acceptors, from two molecules of Ph_3COH.[2] The 1 : 1 adduct **9f** formed by Me_2NCHO possibly uses both the nitrogen and the oxygen atoms as hydrogen-bond acceptors. Surprisingly, no adduct was formed between diol **9** and acetone. Similarly unexpected was the 1 : 2 stoichiometry of the adduct with 1,4-dioxane, where a 1 : 1 adduct analogous to that formed by 4,4′-bipyridyl might have been expected.

When the guest contains OH or NH groups it can in principle act both as hydrogen-bond donor and hydrogen-bond acceptor, so that more complex hydrogen-bonding patterns may occur. Thus with methanol, diol **9** forms a 1 : 1 adduct in which the molecular aggregate is found from the X-ray analysis described below to consist of two molecules each of the diol and methanol joined together by hydrogen bonding describing the motif $\mathbf{R}_6^6(12)$. Diol **4** also forms a 1 : 1 adduct with methanol,[5] possibly of similar constitution, while Ph_3COH forms a 1 : 1 adduct[2] again containing aggregates of two molecules each of Ph_3COH and MeOH joined by hydrogen bonding of type $\mathbf{R}_4^4(8)$. Both **4** and **9** form 1 : 1 adducts also with ethanol, possibly of similar structure to the methanol adducts although crystals of **9**·EtOH have all so far proven to be twinned.

With piperidine $HN(CH_2)_5$ the diol **9** forms a 1 : 2 adduct **9g** and with piperazine, $HN(CH_2CH_2)_2NH$ it forms a 1 : 1 adduct **9i**. In each system the diol and the guest each provide two hydrogen-bond donors and two hydrogen-bond acceptors: there are so many hydrogen-bonding schemes possible for these adducts that, in the absence of structural data, only speculation is possible.

In reactions with mixed liquid guests, diol **9** gives either a single adduct or a mixture of adducts. Thus with MeOH–pyridine, pure **9d** was isolated, although a MeOH–Me_2SO mixture gave the 1 : 1 adduct **9j** rather than the 1 : 2 adduct **9c**. However Me_2SO–dioxane and pyridine–dioxane mixtures gave mixtures of adducts, rather than new molecular adducts containing two different guest molecules.

Preliminary studies using diol **10** have shown no adduct formation with methanol, ethanol or pyridine, while **12** with methanol clearly undergoes more than simple adduct formation as the ^{13}C NMR spectrum of the resulting crystalline product revealed five different phenyl environments and a similar number of cyclopentadienyl environments.

Crystal and Molecular Structures of Adducts **9a** *and* **9d**.—The clathrate complex **9a**, $[Fe(C_5H_4CPh_2OH)_2]\cdot MeOH$, crystallises in the space group $P\bar{1}$ as a centrosymmetric hydrogen-bonded tetrameric assembly which comprises two ferrocene-1,1′-diylbis(diphenylmethanol) host molecules **9** and two guest MeOH molecules. Each methanol molecule is inserted between the hydroxyl groups of the two host molecules forming a centrosymmetric circular twelve-membered $(OH)_6$ ring of hydrogen bonds with motif $\mathbf{R}_6^6(12)$. The oxygen atoms are positioned so as to form the vertices of a distorted chair with unique hydrogen-bonded O···O distances of O(1)···O(2) 2.774(3); O(1)···O(1S′) 2.761(4) Å and O(2)···O(1S′) 2.804(3) Å. Difference-density maps show that within the dimeric aggregate the hydroxyl hydrogen atoms are not disordered (unlike the disordered hydroxyl hydrogens in the crystal structure of the parent host **9** itself, which forms a dimeric aggregate residing on a two-fold axis).[14] The three O–H distances (H-atom coordinates refined isotropically) are 0.77(3), 0.73(3) and 0.78(3) Å, while the three C–O–H angles are 106(3), 114(3) and 122(3)° respectively.

The Fe–C bond lengths in adduct **9a** are in the ranges 2.034(2)–2.057(2) [mean 2.046(3) Å] and 2.032(3)–2.055(2) Å [mean 2.045(2) Å] for the cyclopentadienyl rings C(11)–C(15) and C(21)–C(25) respectively. The C(sp^3)–O bond lengths are 1.440(3) and 1.431(3) Å. The C(sp^3)–C(C_5H_4) bond lengths C(1)–C(15) and C(2)–C(25) are essentially identical, 1.519(3) and 1.518(3) Å, while the C(sp^3)–C(phenyl) distances on either side of the ferrocenyl moiety are similar, 1.536(3), 1.521(3) and 1.536(3), 1.532(4) Å [involving C(1) and C(2) respectively]. The C(C_5H_4)–C(C_5H_4) bond lengths are in the range 1.404(4)–1,428(4) Å [mean 1.419(4) Å], for the cyclopentadienyl ring system C(11)–C(15) and in the range 1.401(4)–1.422(3) Å [mean 1.416(4) Å] for the cyclopentadienyl ring system C(21)–C(25). These values are similar to those reported previously by us in related structures.[13,14] The dihedral angle between the symmetry-related cyclopentadienyl C_5 planes in **9a** is 5.1(1)° and these C_5 rings are within 9.5(2)° of being eclipsed. The conformation adopted is such that the exocyclic C(sp^3) atoms are rotated about a line joining the ring centroids through 59.8(2)° from an eclipsed conformation. These C(sp^3) carbon atoms, C(1) and C(2), are displaced 0.0148(5) and 0.0154(5) Å from the plane of their respective C_5 rings away from the Fe atom.

In the host–guest system of **9a** the host has approximate two-fold symmetry with both of the substituted cyclopentadienyl systems adopting similar conformations as evidenced by the Fe–C(C_5H_4)–C(sp^3)–O torsion angles of 60.2(1)° and 49.0(2)°, involving C(1) and C(2) respectively. Two of the phenyl rings

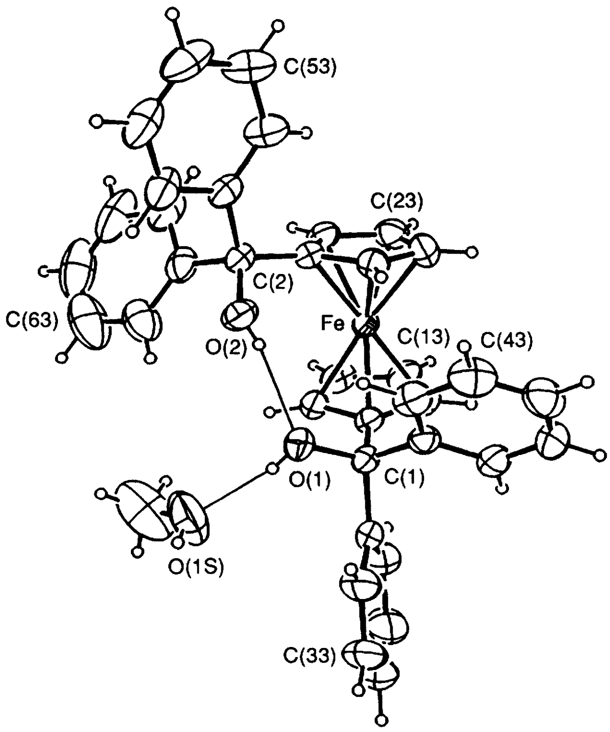


Fig. 1 A view of the asymmetric unit of the host–guest system **9a**, $[Fe(C_5H_4CPh_2OH)_2]\cdot MeOH$, showing the atom-labelling scheme. For clarity the hydrogen atoms are drawn as small spheres of arbitrary size. All non-hydrogen atoms are depicted with their thermal ellipsoids at the 50% level

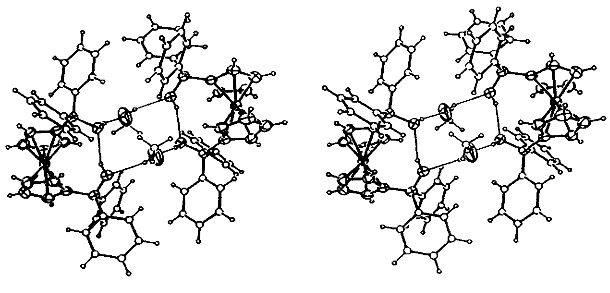


Fig. 2 A stereoview of the centrosymmetric dimeric unit of adduct **9a**: thermal ellipsoids as in Fig. 1

Table 1 Summary of data collection, structure solution and refinement details

(*a*) Crystal data	**9a**	**9d**
Empirical formula	$C_{36}H_{30}FeO_2{\cdot}CH_3OH$	$C_{36}H_{30}FeO_2{\cdot}2C_5H_5N$
M	582.5	708.7
Colour, habit	Yellow, block	Yellow, block
Crystal size/mm	0.25 × 0.40 × 0.65	0.35 × 0.35 × 0.55
Crystal system	Triclinic	Monoclinic
a/Å	8.7624(3)	16.6252(10)
b/Å	12.2797(6)	11.1016(9)
c/Å	14.8773(8)	20.9440(16)
α/°	106.572(4)	90
β/°	97.879(4)	107.855(6)
γ/°	100.873(4)	90
U/Å^3	1475.5(1)	3679.4(5)
Space group	$P\bar{1}$	*C*2/*c*
Z	2	4
Molecular symmetry	None	Two-fold
F(000)	612	1488
D_c/g cm^{-3}	1.31	1.28
μ/mm^{-1}	0.54	0.45
(*b*) Data acquisition[a]		
Unit-cell reflections (2θ range/°)	25 (24–38)	25 (30–40)
hkl range	−12 11, 0 17, −20 20	−23 22, 0 15, 0 29
Variation in three standards	3% decay	< 1% variation
Reflections measured	8569	5460
Unique reflections	8569	5331
R_{int}	—	0.012
Reflections with $I > 3\sigma(I)$	4982	3260
Minimum, maximum, absorption correction	0.827, 0.881	0.785, 0.902
(*c*) Structure solution and refinement[b]		
H-atom treatment	O–H refined, C–H riding	O–H from difference map, C–H 0.95 Å riding
No. of variables	382	231
k in $w = 1/(\sigma^2F_o + kF_o^2)$	0.0003	0.0006
R, R′, S	0.044, 0.047, 1.46	0.042, 0.055, 1.63
Density range in final difference map/e Å^{-3}	−0.35, 0.43	−0.25, 0.39
Final shift/error ratio	< 0.001	< 0.06

[a] Data collection at 21 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatised Mo-Kα radiation (λ = 0.7093 Å); maximum 2θ 60°; absorption correction *via* nine ψ scans. [b] All calculations were done by the Patterson heavy atom method on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs.

Table 2 Positional parameters and their estimated standard deviations (e.s.d.s) for adduct **9a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	0.309 49(4)	0.066 96(3)	0.360 61(2)	C(41)	0.029 76(28)	−0.219 05(20)	0.214 80(16)
O(1)	0.971 98(24)	−0.091 72(16)	0.120 90(14)	C(42)	−0.113 10(32)	−0.189 24(23)	0.223 38(19)
O(2)	−0.003 60(26)	0.117 29(18)	0.208 64(13)	C(43)	−0.217 52(33)	−0.243 39(29)	0.268 74(22)
C(1)	0.150 04(29)	−0.158 89(20)	0.168 89(16)	C(44)	−0.181 67(37)	−0.328 19(28)	0.304 99(21)
C(2)	0.075 71(29)	0.217 72(21)	0.289 27(17)	C(45)	−0.042 03(35)	−0.360 74(23)	0.295 33(20)
C(11)	0.383 85(31)	0.026 60(22)	0.232 69(18)	C(46)	0.062 70(30)	−0.307 39(22)	0.250 54(18)
C(12)	0.516 31(30)	0.074 40(23)	0.310 37(21)	C(51)	−0.055 60(28)	0.274 93(20)	0.324 97(19)
C(13)	0.507 45(30)	0.002 72(23)	0.368 96(20)	C(52)	−0.068 27(33)	0.307 70(25)	0.419 44(21)
C(14)	0.368 99(29)	−0.090 02(21)	0.328 57(18)	C(53)	−0.183 35(38)	0.364 57(29)	0.448 63(24)
C(15)	0.291 95(27)	−0.075 79(20)	0.243 08(16)	C(54)	−0.286 06(36)	0.390 18(26)	0.384 64(30)
C(21)	0.090 69(28)	0.079 79(22)	0.391 27(17)	C(55)	−0.276 35(34)	0.356 64(27)	0.290 12(27)
C(22)	0.193 32(33)	0.075 97(25)	0.472 04(18)	C(56)	−0.161 61(33)	0.300 10(25)	0.260 14(22)
C(23)	0.325 57(33)	0.170 72(25)	0.496 81(18)	C(61)	0.188 87(30)	0.307 05(25)	0.260 35(20)
C(24)	0.306 55(30)	0.234 75(21)	0.432 13(18)	C(62)	0.219 90(37)	0.280 56(33)	0.169 29(24)
C(25)	0.160 54(28)	0.178 00(20)	0.365 72(17)	C(63)	0.316 72(47)	0.367 32(53)	0.143 82(33)
C(31)	0.203 71(32)	−0.250 80(21)	0.094 18(17)	C(64)	0.379 92(45)	0.477 01(47)	0.208 31(44)
C(32)	0.090 21(37)	−0.327 35(25)	0.016 46(20)	C(65)	0.350 26(40)	0.502 23(32)	0.298 01(36)
C(33)	0.130 60(51)	−0.412 45(28)	−0.052 07(22)	C(66)	0.253 91(36)	0.418 62(26)	0.323 96(25)
C(34)	0.283 47(61)	−0.424 08(31)	−0.044 47(27)	O(1S)	0.201 06(45)	−0.043 95(30)	−0.026 83(19)
C(35)	0.397 61(48)	−0.349 55(35)	0.032 36(27)	C(1S)	0.315 44(61)	0.040 78(60)	−0.037 02(33)
C(36)	0.357 79(37)	−0.262 06(27)	0.101 46(21)				

are almost normal to the ferrocenyl system as evidenced by the angles C(31)–C(1)–C(15)–C(11) 86.4(2), C(31)–C(1)–C(15)–C(14) −86.0(2), C(51)–C(2)–C(25)–C(21) 72.6(2)°, and C(51)–C(2)–C(25)–C(24) −98.2(2)°. These two phenyl rings (one on each substituted cyclopentadienyl ring system) are also oriented so that they are almost parallel to the exocyclic C(1)–C(31) or C(2)–C(51) bond, with C(15)–C(1)–C(31)–C(32) −174.5(2) and C(25)–C(2)–C(51)–C(52) 13.2(1)°. The other two phenyl

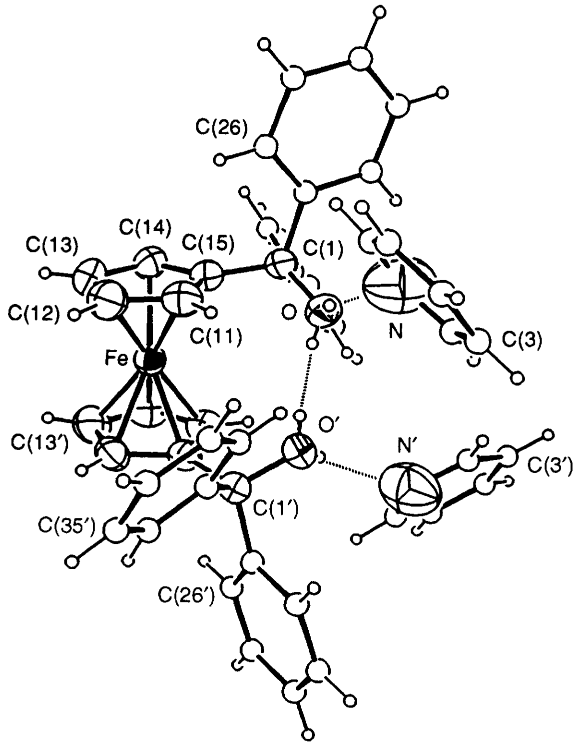


Fig. 3 A view of the host–guest system **9d**, $[Fe(C_5H_4CPh_2OH)_2]\cdot 2C_5H_5N$, showing the atom-labelling scheme. For clarity, the carbon and hydrogen atoms are drawn as small spheres of arbitrary size

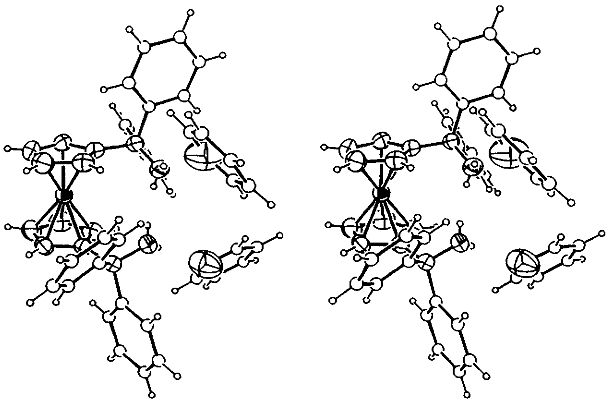


Fig. 4 A stereoview of adduct **9d**

Table 3 Positional parameters and their e.s.d.s for adduct **9d**

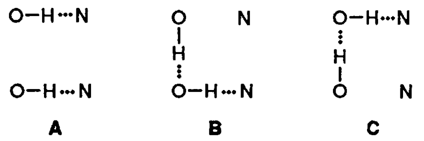
Atom	*x*	*y*	*z*
Fe	0.500 00	0.292 70(4)	0.250 00
O	0.584 41(9)	−0.004 38(13)	0.292 37(8)
C(1)	0.644 33(12)	0.091 17(17)	0.310 08(10)
C(11)	0.527 38(13)	0.210 14(21)	0.341 43(10)
C(12)	0.505 44(16)	0.332 51(24)	0.346 22(12)
C(13)	0.562 88(15)	0.404 71(21)	0.326 09(13)
C(14)	0.620 37(13)	0.328 15(20)	0.308 34(11)
C(15)	0.598 94(11)	0.206 68(18)	0.317 51(9)
C(21)	0.708 89(12)	0.054 26(18)	0.377 28(10)
C(22)	0.760 58(16)	−0.044 39(23)	0.377 65(13)
C(23)	0.815 86(17)	−0.086 61(27)	0.437 50(15)
C(24)	0.821 21(17)	−0.030 85(28)	0.496 68(14)
C(25)	0.771 55(17)	0.066 88(25)	0.497 22(12)
C(26)	0.714 94(15)	0.109 55(21)	0.437 37(11)
C(31)	0.688 38(13)	0.102 88(19)	0.256 03(10)
C(32)	0.659 83(16)	0.040 12(23)	0.196 33(12)
C(33)	0.699 68(24)	0.053 47(32)	0.147 47(14)
C(34)	0.767 68(25)	0.128 06(37)	0.157 51(18)
C(35)	0.798 11(19)	0.188 95(29)	0.217 06(19)
C(36)	0.758 76(15)	0.176 11(23)	0.266 41(13)
N	0.546 57(24)	−0.169 12(44)	0.388 79(22)
C(2)	0.502 15(34)	−0.265 28(56)	0.365 22(26)
C(3)	0.457 73(28)	−0.322 44(39)	0.399 86(40)
C(4)	0.461 78(30)	−0.274 21(58)	0.463 22(38)
C(5)	0.509 19(36)	−0.180 56(45)	0.485 89(23)
C(6)	0.551 26(28)	−0.132 43(37)	0.448 33(23)

rings attached at C(41) and C(61) are oriented *exo* to the central core of the centrosymmetric O–H ··· O hydrogen-bonding array with C(15)–C(1)–C(41)–C(42) 106.0(2) and C(25)–C(2)–C(61)–C(62) 114.6(2)°. The orientations of the phenyl ring systems are similar to those observed in the crystal structure determination of the parent host **9** itself.[14] The O–C(sp^3)–C(aromatic) angles about the central C(sp^3) carbons C(1) and C(2) differ considerably as evidenced by O(1)–C(1)–C(31) 108.6(2), O(1)–C(1)–C(41) 107.5(2) and O(2)–C(2)–C(51) 105.6(2), C(2)–C(2)–C(61) 111.5(2)°. These differences presumably arise because of the slightly different hydrogen-bonding environments at O(1) and O(2) and intermolecular packing forces.

Weber *et al.*,[20] in a systematic study of crystalline inclusion compounds of tartaric acid-derived hosts and alcohol guests, have recently reported a similar type of O–H ··· O hydrogen-bonding arrangement to that of the host–guest system **9a** which also involves two host molecules and two methanol guest molecules forming a 12-membered centrosymmetric hydrogen-bonded tetrameric assembly. However, the central O–H ··· O hydrogen-bonded core in our structure **9a** is more distorted, presumably because of the relative orientation of the hydroxyl groups.

The host : guest system **9d**, $[Fe(C_5H_4CPh_2OH)_2]\cdot 2C_5H_5N$, crystallises in the space group *C*2/*c*, with the ferrocenyl host molecule residing on a two-fold axis (which passes through the iron atom), and involved in O–H ··· N hydrogen bonding with two pyridine molecules. Difference-density maps showed that within the aggregate of **9d** the hydroxyl hydrogen atoms of the diol are disordered equally over two sites, one directed towards the two-fold symmetry-related neighbouring hydroxyl oxygen atom and the other towards the pyridine nitrogen atom as depicted in Figs 3 and 4. The distance between the two-folded symmetry-related hydroxyl oxygen atoms O ··· O' is 2.824(3) Å while the O ··· N distance is 2.932(4) Å. Fourier difference maps in the plane of the pyridine ring system in the final stages of refinement indicated that this ring was not disordered. The two O–H distances (H-atom coordinates from difference maps) are 0.73 and 0.70 Å, and the two C–O–H angles are 116.6 and 121.4° (H–O–H 89°).

The hydrogen bonding in adduct **9d** is worth considering in a little more detail. If it is assumed that the two hydrogen sites between the oxygen atoms are not simultaneously occupied, then three possible hydrogen-bond arrangements (**A**–**C**) can be envisaged. For equal population of the four hydrogen sites, in a static system, only arrangements **B** and **C** can be involved. In each of **B** and **C** only one pyridine is actually hydrogen bonded to the diol: since there seems no reason to exclude **A**, a more plausible model of the hydrogen bonding involves rapid jumps of the hydrogen atoms, each between two sites, as found for the parent diol **9** itself.[17]



The Fe–C bond lengths in adduct **9d** are in the range 2.038(2)–2.047(2) Å [mean 2.041(2) Å] for the unique

Table 4 Selected dimensions (lengths in Å, angles in °) for adduct **9a**

Fe–C(11)	2.053(3)	Fe–C(12)	2.049(3)	Fe–C(3)	2.039(3)
Fe–C(14)	2.034(2)	Fe–C(15)	2.057(2)	Fe–C(21)	2.055(2)
Fe–C(22)	2.049(3)	Fe–C(23)	2.032(3)	Fe–C(24)	2.038(2)
Fe–C(25)	2.051(2)	O(1)–C(1)	1.440(3)	O(2)–C(2)	1.431(3)
C(1)–C(15)	1.519(3)	C(1)–C(31)	1.536(3)	C(1)–C(41)	1.521(3)
C(2)–C(25)	1.518(3)	C(2)–C(51)	1.536(3)	C(2)–C(61)	1.532(4)
C(11)–C(12)	1.420(4)	C(11)–C(15)	1.420(3)	C(12)–C(13)	1.404(4)
C(13)–C(14)	1.421(4)	C(14)–C(15)	1.428(3)	C(21)–C(22)	1.417(4)
C(21)–C(25)	1.421(3)	C(22)–C(23)	1.401(4)	C(23)–C(24)	1.418(4)
C(24)–C(25)	1.422(3)	C(31)–C(32)	1.386(4)	C(31)–C(36)	1.376(4)
C(32)–C(33)	1.374(4)	C(33)–C(34)	1.366(7)	C(34)–C(35)	1.374(7)
C(35)–C(36)	1.394(4)	C(41)–C(42)	1.381(4)	C(41)–C(46)	1.396(3)
C(42)–C(43)	1.389(4)	C(43)–C(44)	1.368(5)	C(44)–C(45)	1.370(4)
C(45)–C(46)	1.380(4)	C(51)–C(52)	1.374(4)	C(51)–C(56)	1.386(4)
C(52)–C(53)	1.381(4)	C(53)–C(54)	1.363(5)	C(54)–C(55)	1.367(6)
C(55)–C(56)	1.379(4)	C(61)–C(62)	1.378(4)	C(61)–C(66)	1.384(4)
C(62)–C(63)	1.406(6)	C(63)–C(64)	1.370(9)	C(64)–C(65)	1.354(8)
C(65)–C(66)	1.380(4)	O(1S)–C(1S)	1.359(7)		

O(1) · · · O(2)	2.774(3)	O(1) · · · O(1S′)	3.518(4)	O(1) · · · O(1S)	2.761(4)
O(2) · · · O(1S′)	2.804(3)	O(1S) · · · O(1S′)	3.992(7)	O(1) · · · O(1)	4.905(3)
O(2) · · · O(2)	6.068(3)				

O(1)–H(1)	0.77(3)	O(2)–H(2)	0.73(3)	O(1S)–H(3)	0.78(3)
O(1) · · · H(2)	2.10(3)	O(1S) · · · H(1)	2.00(3)	O(2) · · · H(3′)	2.10(3)

O(2) · · · O(1) · · · O(1S)	102.0(1)	O(2) · · · O(1)–H(1)	109(3)
O(1S) · · · O(1) · · · H(2)	102(1)	H(1)–O(1) · · · H(2)	109(3)
C(1)–O(1)–H(1)	106(3)	C(1)–O(1) · · · H(2)	121(1)
O(1) · · · O(2) · · · O(1S′)	78.2(1)	O(1) · · · O(2) · · · H(3′)	82(1)
C(2)–O(2)–H(2)	114(3)	C(2)–O(2) · · · H(3)	137(1)
H(2)–O(2) · · · H(3′)	98(3)	O(1) · · · O(1S) · · · O(1′)	102.1(1)
O(1) · · · O(1S) · · · O(2′)	118.0(1)	O(1) · · · O(1S)–H(3)	99(2)
O(1′) · · · O(1S) · · · H(1)	105(1)	O(2′) · · · O(1S) · · · H(1)	119(1)
O(1)–H(1) · · · O(1S)	167(4)	O(1) · · · H(2)–O(2)	153(3)
O(2′) · · · H(3)–O(1S)	149(3)		

Primes represent the symmetry-related equivalent position $-x, -y, -z$.

Table 5 Selected dimensions (lengths in Å, angles in °) for adduct **9d**

Fe–C(11)	2.044(2)	Fe–C(12)	2.038(2)	Fe–C(13)	2.039(2)
Fe–C(14)	2.038(2)	Fe–C(15)	2.047(2)	O–C(1)	1.424(2)
C(1)–C(15)	1.520(3)	C(1)–C(21)	1.541(3)	C(1)–C(31)	1.531(3)
C(11)–C(12)	1.418(3)	C(11)–C(15)	1.426(3)	C(12)–C(13)	1.407(4)
C(13)–C(14)	1.412(3)	C(14)–C(15)	1.423(3)	C(21)–C(22)	1.391(3)
C(21)–C(26)	1.376(3)	C(22)–C(23)	1.389(3)	C(23)–C(24)	1.364(4)
C(24)–C(25)	1.365(4)	C(25)–C(26)	1.399(3)	C(31)–C(32)	1.382(3)
C(31)–C(36)	1.386(3)	C(32)–C(33)	1.387(4)	C(33)–C(34)	1.365(7)
C(34)–C(35)	1.372(6)	C(35)–C(36)	1.390(4)	N–C(2)	1.306(8)
N–C(6)	1.291(7)	C(2)–C(3)	1.343(10)	C(3)–C(4)	1.413(12)
C(4)–C(5)	1.303(9)	C(5)–C(6)	1.316(6)		

O · · · O′	2.824(3)	O · · · N	2.932(4)	O–H(1A)	0.725
O–H(1B)	0.697	O · · · H(1B)	2.14		

O′ · · · O–C(1)	130.1(1)	O′ · · · O–N	92.9(1)	N · · · O–H(1B′)	95.2	H(1A)–O–H(1B)	89.2
O′ · · · O–H(1A)	87.5	N · · · O–H(1B)	97.4	O–H(1A) · · · N	154.8	O–H(1B) · · · O	167.5

Primes represent the symmetry-related equivalent position $1 - x, y, \frac{1}{2} - z$.

substituted cyclopentadienyl ring system C(11)–C(15). The C(sp^3)–O bond length is 1.424(2) Å which compares favourably with previously determined structures. The C(C_5H_4)–C(C_5H_4) bond lengths are in the range 1.407(4)–1.426(3) Å [mean 1.417(3) Å]. The dihedral angle between the symmetry-related C_5 planes in the molecule is 3.1(1)° and these C_5 rings are within 2.3(1)° of being eclipsed. The conformation adopted by the host molecule is such that the two-fold symmetry-related exocyclic C(sp^3) atoms are rotated about a line joining the ring centroids through 66.8(1)° from an eclipsed conformation. The C(sp^3) carbon atom C(1) is displaced 0.091(4) Å from the plane of the cyclopentadienyl C_5 ring system and away from the Fe atom.

The two unique phenyl rings adopt similar orientations to the related phenyl groups of the host in **9a**. One phenyl ring is oriented so that it is almost parallel to the exocyclic C(1)–C(21) bond with C(15)–C(1)–C(21)–C(22) −174.9(2)°; this phenyl ring is also almost normal to the ferrocene system with C(21)–C(1)–C(15)–C(11) −83.4(2)°. The other phenyl ring attached at C(31) is oriented *exo* to the central core of the O–H · · · O and O–H · · · N hydrogen-bonding array with C(15)–C(1)–C(31)–C(32) −110.9(2) and C(31)–C(1)–C(15)–C(11) 153.5(2)°.

Weber *et al.*[21] have reported the structure of a crystalline host–guest system involving 2,2′-bis(hydroxydiphenylmethyl)-1,1′-binaphthyl and pyridine (1:3), where one of the host hydroxyl groups is involved in an intramolecular O–H···O hydrogen bond [O···O 2.68; 2.824(3) Å in **9d** above], and the other hydroxyl group participates in an intermolecular O–H···N hydrogen bond with a pyridine guest molecule [O···N 2.78; 2.932(4) Å in **9d**]. The other two pyridine molecules are not involved in any form of hydrogen bonding and are present in cavities between the host molecules. This host–guest system[21] is very different from **9d**. The O···O and O···N hydrogen-bonding distances are considerably longer in **9d** than in the binaphthyl system and this probably facilitates the hydroxyl O–H···O/O–H···N disorder and hydrogen-bonding host:guest ratio of 1:2 in **9d**.

We have also previously examined the methanol[22] and ethanol[23] clathrate structures of calix[4]arenes in which the alcohol is *exo* to[22] (methanol O–H···O intermolecular hydrogen bonding) or enclathrated within the calixarene molecular cavity[23] [ethanol C–H···C(arene) interactions].

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