Hydrogen-bonded Adducts of Ferrocene-1,1′-diylbis(diphenylmethanol): Crystal and Molecular Structures of 1:1 Adducts with 4,4′-Bipyridyl, Piperazine and Dimethylformamide, the 2:1:1 Hydrated Adduct with Morpholine, and Two Adducts with 1,4-Dioxane, 1:1 at 150 K and 1:2 at 298 K†

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Host–guest adducts formed by ferrocene-1,1′-diylbis(diphenylmethanol) **1** with oxygen- and/or nitrogen-containing guests exhibited a wide range of hydrogen-bonding patterns as determined by X-ray crystallography. The 1 : 1 adduct **2** formed with 4,4′-bipyridyl comprises a centrosymmetric hydrogen-bonded aggregate involving two molecules of the diol and one of the bipyridyl and contains intramolecular O–H ··· O and intermolecular O–H ··· N hydrogen bonds; the second molecule of the bipyridyl, also centrosymmetric, is trapped in a cavity, but is not hydrogen bonded to any other part of the structure. The structure of the 1 : 1 adduct formed with piperazine **3** is chiral and consists of infinite spiral chains, with alternating diol and piperazine molecules, which contain only O–H ··· N hydrogen bonds. Morpholine forms both anhydrous **4a** and hydrated adducts **4b** with the host diol, both having host : guest ratios of 2 : 1: the hydrated adduct contains infinite ribbons comprising ferrocene units on the outside edges and disordered water and morpholine components in the body of the ribbon. With 1,4-dioxane a 1 : 1 **5a** and a 1 : 2 adduct **5b** are formed. The centrosymmetric hydrogen-bonded aggregate of **5a** consists of two molecules of the diol and one of dioxane and contains both intra- and inter-molecular O–H ··· O hydrogen bonds: the second dioxane molecule is also centrosymmetric and is trapped in a structural cavity and not bonded to the rest of the structure. Adduct **5b** is isomorphous with the 1 : 2 diol : pyridine adduct. The diol component lies on a two-fold rotation axis, forming hydrogen bonds to the dioxane molecules which are highly disordered and readily lost from the structure. In the 1 : 1 complex formed with dimethylformamide **6** inter- and intra-molecular O–H ··· O hydrogen bonds link a finite host–guest pair, which also includes an intermolecular C–H ··· π(arene) interaction. The hydrogen-bonding patterns are analysed and codified using a graph-set approach.

Organic diols of type $[RR'C(OH)]_2X$ (where R,R′ represent phenyl or large aryl substituents and X is a spacer group of generally limited flexibility) have proven to be versatile hosts for the capture of a wide range of guest molecules.[1] The guests can be hydrogen-bond acceptors or hydrogen-bond donors and in most, but not all,[1k] cases, the guest is bound to the host by hydrogen bonds.

We have recently initiated a study of host–guest complexation using hosts containing the electroactive ferrocene nucleus. The diol ferrocene-1,1′-diylbis(diphenylmethanol),[2] $[Fe(C_5H_4CPh_2OH)_2]$ **1**, forms[3] adducts with a wide range of hydrogen-bond donors and acceptors, and we have previously shown[3] that the 1 : 1 adduct with methanol forms cyclic aggregates containing two molecules of the diol host and two molecules of the guest methanol, hydrogen bonded to form a chair conformation $(OH)_6$ ring, and that in the 1 : 2 adduct with pyridine the diol has the hydroxyl hydrogen disordered and participating in both intramolecular O–H ··· O and intermolecular O–H ··· N hydrogen bonds.

For guests which contain more than one hydrogen-bond donor or acceptor group the possible patterns of hydrogen bonding between the diol **1** and such guests become both more numerous and more complex. For example, 4,4′-bipyridyl (bipy), which can normally act only as a hydrogen-bond acceptor, forms an adduct **2** of 1 : 1 host : guest stoichiometry, for which both macrocyclic ('box') and long-chain formulations were suggested:[3] in fact the structure reported here for adduct **2** from X-ray diffraction data shows that neither of the earlier speculative suggestions of box or chain formulations was in fact correct.

Piperazine (pipz), which is potentially both a donor and an acceptor of hydrogen bonds, also forms[3] a 1 : 1 adduct **3**: the structure reported here shows that in this adduct piperazine acts only as an acceptor of hydrogen bonds, not as a donor. Morpholine (morph) is similarly both a potential donor and acceptor of hydrogen bonds: we have characterised both a 2 : 1 adduct **4a** and its hydrate **4b**, of composition 2 : 1 : 1, and have determined the crystal and molecular structure of the latter. Completing this series of six-membered ring heterocycles is 1,4-dioxane (diox) which forms an adduct which is rather unstable

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

at room temperature, but structures of both a 1:1 adduct **5a** and a 1:2 adduct **5b** have now been determined.

Dimethylformamide (dmf) contains two potential hydrogen-bond acceptor sites, of which the oxygen atom could act as acceptor of either one or two hydrogen bonds. The structure of the 1:1 adduct **6** formed[3] between Me_2NCHO and the diol **1** has now been determined: the Me_2NCHO guest acts as acceptor of a single intermolecular hydrogen bond of type O–H··· O and as donor of an intramolecular C–H···π (arene) hydrogen bond.

The adduct structures reported here, together with those reported earlier for adducts with methanol and with pyridine, bring to eight the number of adducts of the ferrocenediol **1** to have been structurally characterised by X-ray methods. A wide range of crystal structures occur in this series, and no one structure type is predictable from knowledge of the remainder: in particular the hydrogen-bond donor and/or acceptor behaviour of the guest components is not yet readily predictable. However analysis of the hydrogen-bonding patterns reveals some common themes, and these are described using graph-set methods.

Experimental

Crystalline samples of the 4,4′-bipyridyl, piperazine, dioxane and dimethylformamide adducts **2**, **3**, **5** and **6** were prepared as previously described.[3] A crystalline sample of the anhydrous morpholine adduct **4a** was prepared by dissolution of a sample of compound **1** in an excess of dried redistilled morpholine, followed by slow evaporation of the solvent, to provide orange-yellow crystals, which were dried over calcium chloride (Found: C, 76.7; H, 5.5; N, 1.1. $C_{76}H_{69}Fe_2NO_5$ requires C, 76.8; H, 5.8; N, 1.2%). NMR ($CDCl_3$): ^1H, δ 2.84 (m, 4 H) and 3.66 (m, 4 H) (morpholine), 3.94 (m, 8 H) and 4.14 (m, 8 H) ($4C_5H_4$), 4.4 (br s, 4OH), and 7.2–7.3 (m, 40 H, $8C_6H_5$); ^{13}C, δ 46.4 (t, CH_2N), 68.4(d), 69.4(d) and 97.3(s) (C_5H_4), 78.2 (s, COH), 126.8(d), 127.1(d), 127.5(d) and 147.4(s) (C_6H_5). The hydrated morpholine adduct **4b** was obtained either by exposure of the anhydrous adduct to air for a few hours, or by slow evaporation of a solution of the diol in wet morpholine (Found: C, 76.1; H, 6.5; N, 1.2. $C_{76}H_{71}Fe_2NO_6$ requires C, 75.7; H, 5.9; N, 1.2%). The composition was confirmed by X-ray structure analysis.

Thermal Analyses.—The DSC measurements were made using a Perkin-Elmer model DSC-7 instrument, with a heating rate of 10 °C min^{-1}: TGA measurements were made using a Stanton-Redcroft model TR-1 thermobalance.

X-Ray Crystallography.—Crystals of the adducts **2**, **3**, **4b**, **5** and **6** were selected directly from the prepared samples. Details of the X-ray experimental conditions, cell data, data collection and refinements are summarised in Table 3.

All structures were solved by the heavy-atom method: all hydrogen atoms bonded to carbon were clearly visible in difference maps and were allowed for as riding atoms, with C–H 0.95 Å. All hydroxyl hydrogen atoms, and hydrogen bonded to nitrogen in **3**, were located from difference maps. In each case, 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 **2** crystallised in the triclinic system, with space group $P1$ or $P\bar{1}$: the latter was chosen and confirmed by successful refinement. System **3** crystallised in the monoclinic system and the space group was determined from the systematic absences ($0k0$ absent if $k = 2n + 1$) which allows $P2_1$ or $P2_1/m$: the former was selected from the value of Z and confirmed by successful analysis.

Adduct **4b** crystallised in the triclinic system, space groups $P\bar{1}$ or $P1$: the former was assumed and confirmed by successful analysis. The structure solution revealed that the morpholine molecule adopted two orientations about a centre of inversion, offset from the ring centre, such that two carbon positions were common to the two orientations: in addition the two heteroatoms in the morpholine are each equally distributed over two sites as judged by the refined site occupancies, giving orientational disorder in addition to positional disorder. There is also a water molecule, also disordered over two sites related by a centre of inversion. Owing to the disorder it was not possible to locate the hydrogen atoms of the water molecule and the NH group. The hydroxyl hydrogen atoms of the ferrocene diol component are also disordered, one over two sites and the other over three. The treatment of hydrogen bound to carbon and the rest of the refinement, was as for **2**. When the entire refinement was repeated in space group $P1$ with the morpholine and water components ordered, rather than disordered as in $P\bar{1}$, the refinement converged to $R = 0.049$ (*cf.* $R = 0.043$ in $P\bar{1}$), and the highest peaks in the final difference map corresponded to the symmetry-related morpholine and water molecules; the *R* values and the difference map both serve to confirm $P\bar{1}$ rather than $P1$ as the correct space group.

The initial sample of the dioxane adduct gave crystals which were monoclinic (denoted **5b**): the space group was determined from the systematic absences (hkl absent if $h + k = 2n + 1$; $h0l$ absent if $l = 2n + 1$) as Cc or $C2/c$; $C2/c$ was indicated by the *E* statistics and confirmed by the analysis. Diffraction data were collected rapidly from a crystal coated in epoxy resin, but even after 12 h considerable deterioration of the crystal had occurred. The unit-cell data and the subsequent structure solution based on this data set showed that the diol:dioxane ratio was 1:2, with the diol component lying on a two-fold axis and the dioxane component in a general position. The dioxane molecule was found to be severely disordered, and to give low refined site-occupation factors (in the range 0.62–0.82), consistent with loss of dioxane during the data collection.

A second crystal was therefore selected from a freshly prepared sample, coated with epoxy resin and rapidly cooled to 150 K. This crystal (denoted **5a**) proved to be triclinic, space group $P1$ or $P\bar{1}$: the latter was chosen and confirmed by the subsequent successful analysis. Despite the low-temperature data collection and the epoxy coating, significant crystal decay did occur. The analysis showed that in **5a** the diol:dioxane ratio is 1:1, rather than 1:2 as found for **5b**. When a crystal from this batch was examined at ambient temperature the unit-cell dimensions and space group confirmed that it was identical with the crystal studied at 150 K. Hence two different adducts occur.

The 1:1 adduct **6** formed between the diol **1** and dimethylformamide crystallises in the monoclinic system: the space group was established uniquely as $P2_1/c$ from the systematic absences ($h0l$ absent if $l = 2n + 1$; $0k0$ absent if $k = 2n + 1$).

All figures were prepared with the aid of ORTEP II[5] and PLUTON.[6]

Refined atomic coordinates for compounds **2**, **3**, **4b**, **5a**, **5b** and **6** are in Table 4: selected molecular dimensions are in Table 2. Figs. 1–3 and 5–7 show perspective views of the structures, with the atom labelling schemes: Fig. 4 shows the disorder of the morpholine and water components of **4b**.

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

Results and Discussion

Host–Guest Complexes.—We have previously[3] characterised the adducts **2**, **3** and **6** formed by the ferrocenediol **1** with 4,4′-bipyridyl, piperazine and dimethylformamide respectively: all were found to have host:guest ratios of 1:1, based upon both microanalytical and ^1H NMR data. No sound structural deductions could be made from the evidence available in the earlier work,[3] but structures of these adducts determined by X-ray analysis are described below.

In the same work[3] we also found evidence for a very unstable adduct formed between the diol **1** and 1,4-dioxane. No reproducible microanalysis could be obtained for it, probably because of the great ease with which the dioxane is lost, although integrated ^{1}H NMR spectra suggested a diol : dioxane ratio of 1 : 2. X-Ray diffraction data have now led to the characterisation of two well defined diol : dioxane adducts. One of these has a host : guest ratio of 1 : 2, as indicated by NMR data, although this phase readily loses dioxane: a second adduct has now been characterised with a host : guest ratio of 1 : 1.

With anhydrous morpholine, the diol **1** forms an adduct **4a** characterised by microanalytical and ^{1}H NMR data as having a diol:guest ratio of 2 : 1. Upon exposure to air, it rapidly absorbs one molecule of water per morpholine to produce the hydrated adduct **4b** of 2 : 1 : 1 composition. The same material is formed when the diol **1** is crystallised directly from wet morpholine, and the structure of this hydrated phase is described below.

DSC Measurements.—Adducts of the diol **1** with guests which are liquids at room temperature all showed, in addition to an endotherm around 185 °C (which corresponds to the melting temperature of the free diol), an endotherm at lower temperatures which can be identified,[1f,m,7] with loss of the guest molecules from the host–guest array. It has been suggested[8] that the parameter $\Delta T = T_{on} - T_b$ (where T_{on} is the onset temperature of the endotherm for guest loss, and T_b is the normal boiling point of the guest) is a useful indicator of compound stability.

For complexes formed by liquid guests with the host diol **1**, those with dmf, dimethyl sulfoxide (dmso), piperidine and dioxane all lose the guest component at temperatures well below the normal guest boiling point (Table 1), while the pyridine complex loses its guest component at the normal boiling point. The hydrated morpholine complex **4b** shows two endotherms with onset temperatures of 93 and 149 °C, corresponding to loss of water and morpholine respectively, as shown by TGA measurements: of these the temperature for morpholine loss is 20 °C above the normal boiling point. For the 1 : 1 complexes formed by methanol and ethanol the ΔT values are 59 and 11 °C respectively, indicative of particular thermal stability for the methanol complex. An even larger ΔT value (82 °C) has been reported[9] for the 1 : 2 methanol adduct with 1,1′-binaphthyl-2,2′-dicarboxylic acid, although the ΔT value for the corresponding ethanol complex was only 10 °C.

Crystal and Molecular Structures of Adducts **2**, **3**, **4b**, **5a**, **5b** *and* **6**.—*Bipyridyl adduct* **2**. The diol **1** forms an adduct **2** with 4,4′-bipyridyl which has 1 : 1 stoichiometry. This stoichiometry provides an excess of hydrogen-bond acceptors over hydrogen-bond donors: both the nitrogen atoms of the amine and the oxygen atoms of the diol[2] can, in principle, act as hydrogen-bond acceptors, while the number of hydrogen-bond donors is only half the number of acceptors. In the 1 : 2 adduct formed[3] between the diol **1** and pyridine a similar mismatch between the number of donors and acceptors is accommodated by mobility of hydrogen atoms between intermolecular O–H ··· O hydrogen bonds.

In adduct **2** a hydrogen-bonding strategy is adopted different from that in the pyridine adduct. The hydrogen-bonded aggregate (Fig. 1) consists of two molecules of the diol and one of 4,4′-bipyridyl, lying across a centre of inversion at $\frac{1}{2}$, 0, $\frac{1}{2}$: the diol forms intermolecular O–H ··· N and intramolecular O–H ··· O hydrogen bonds, such that all the hydroxyl hydrogens are ordered, with a perfect match of hydrogen-bond donors and acceptors within this aggregate. The second 4,4′-bipyridyl molecule, which also lies across a centre of inversion, at 0, $\frac{1}{2}$, $\frac{1}{2}$ participates in no hydrogen-bonded aggregates. A stereoview of the unit-cell contents is shown in Fig. 8. Similar structural versatility on the part of 4,4′-bipyridyl has been observed previously in its 1 : 1 adduct with [Ni^{II}{(dmg)BF$_2$}$_2$][10] (dmg = dimethylglyoximate), where half of the bipyridyl molecules serve as bridging ligands connecting dimeric [{Ni[(dmg)BF$_2$]$_2$}$_2$] units into infinite chains, while the other half lie trapped in cavities between the chains, but not bonded to the chains.

Table 1 The DSC data for guest-loss processes in adducts of compound **1** with liquid guests

Guest	T_{on}/°C	ΔT/°C
MeOH	124	+59
EtOH	89	+11
dmso	138	−51
Pyridine	112	≈0
1,4-Dioxane	62	−40
dmf	115	−38
Piperidine	62	−44
Morpholine/water	93	−7 (loss of water)
	149	+20 (loss of morpholine)

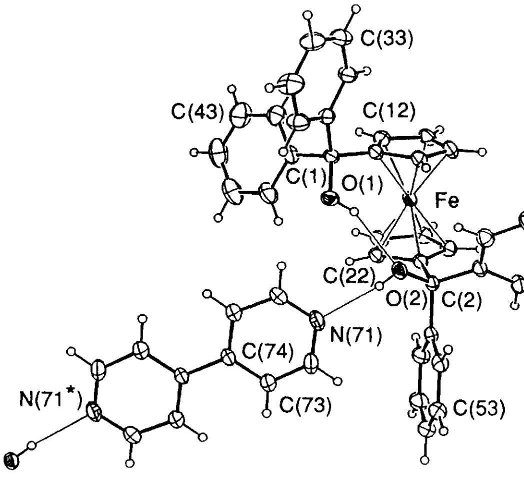

Fig. 1 View of the hydrogen-bonded aggregate in the host–guest system **2**, showing the atom-labelling scheme. For clarity, the hydrogen atoms are shown as small spheres of arbitrary size: non-hydrogen atoms are depicted with their thermal ellipsoids at the 35% level. The non-bonded guest molecule, not shown, comprises the atoms N(81), C(82)–C(86) and their symmetry-related counterparts

The dimensions of the free and the hydrogen-bonded bipyridyl molecules are similar except for the C–N bonds and the inter-ring bond which are both significantly shorter in the free molecule: in both molecular types the rings are parallel as both lie across centres of inversion. In the 4,4′-bipyridyl adduct of [Ni{(dmg)BF$_2$}$_2$][10] the precision of the determination does not allow any metrical comparison to be made between the free and the complexed bipyridyl fragments. Although neither appears to differ significantly in bond lengths from the structures reported here, neither is planar: each lies in a site of crystallographic 222 symmetry (D_2), with inter-ring twist angles of 40 and 34° for the free and co-ordinated molecules respectively.[10]

Piperazine adduct **3**. In the piperazine adduct **3** the diol host component **1** and the piperazine guest each contain two potential hydrogen-bond donor sites and two potential hydrogen-bond acceptor sites per molecule. The X-ray analysis shows however that the diol acts only as a donor, and the piperazine only as an acceptor, so that the hydrogen bonds present are all of the type O–H ··· N: the N–H bonds take no part in the hydrogen-bonding scheme. The diol adopts an approximately transoid conformation of the two C$_5$H$_4$CPh$_2$OH fragments, each of which forms a single O–H ··· N hydrogen bond to a different piperazine molecule: the piperazine adopts a chair conformation having one NH bond axial and the other equatorial, with each nitrogen atom accepting a hydrogen bond

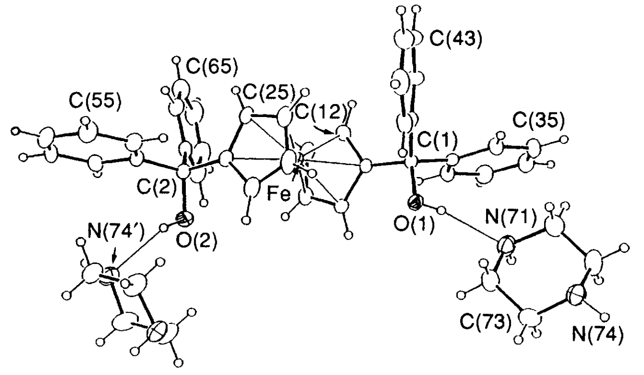

Fig. 2 Section of the infinite spiral chain in the adduct **3**, showing the atom-labelling scheme: the atoms are depicted as in Fig. 1

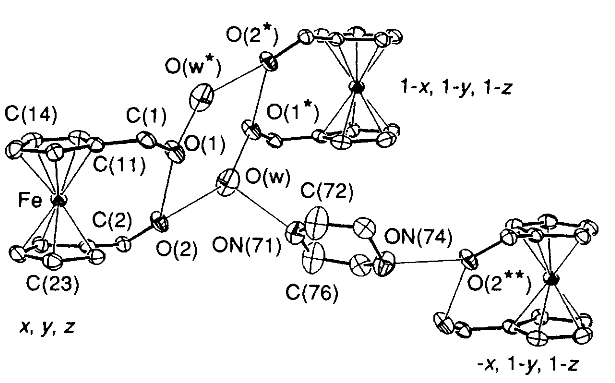

Fig. 3 Portion of the ribbon structure of adduct **4b**, with the phenyl groups omitted for the sake of clarity. The basic motif consists of the two asymmetric units at *x*, *y*, *z* and $-x$, $1-y$, $1-z$ for which only one of the two disordered orientations is shown for the water and morpholine molecules. Part of another asymmetric unit, translated along *a* to $1-x$, $1-y$, $1-z$ is shown to illustrate the formation of ribbons parallel to *a*. The atom-labelling scheme is indicated, as are the hydrogen-bonding sites. The atoms are drawn as in Fig. 1

from a different diol molecule. The diol and piperazine components thus alternate along an infinite chain (Fig. 2) which forms a spiral around a crystallographic 2_1 axis.

Uniquely amongst all the adducts of the diol **1** so far studied, **3** is chiral, although self-assembled from achiral components: all the others crystallize in centrosymmetric space groups. When the final refinement for **3** was performed for both enantiomers, the resulting *R* and *R'* values were 0.032 and 0.041 (*R*), and 0.041 and 0.058 (*R'*). A portion of the infinite spiral structure of the appropriate chirality is shown in Fig. 2, and a stereoview of the unit-cell contents in Fig. 9.

The observation that piperazine acts solely as an acceptor of hydrogen bonds enables us to speculate that in the 1:2 adduct formed[3] by the diol **1** with piperidine, a similar pattern of hydrogen bonds will occur, with each hydroxyl group of the diol acting as a hydrogen-bond donor to the nitrogen atom of one piperidine molecule.

Within the piperazine portion in adduct **3** the C–C bond lengths are 1.487(6) and 1.505(6) Å (mean 1.496 Å) and the C–N bond lengths range from 1.450(6) to 1.476(6) Å (mean 1.460 Å). These values may be compared with those recorded[11] in the gas phase for isolated molecules, also in the chair conformation but with both NH bonds equatorial and forming no hydrogen bonds: C–C 1.540(8) and C–N 1.467(4) Å. The observation here of one equatorial and one axial NH reflects the very low (*ca.* 1.5 kJ mol^{-1}) preference for equatorial over axial NH sites:[12] hydrogen-bond energies exceed by several-fold this site-preference energy difference.

Morpholine adduct **4b**. In the structure of the hydrated morpholine adduct **4b** the asymmetric unit consists of one molecule of the ferrocenediol **1**, one-half of a morpholine molecule and one-half of a water molecule. The structure is elaborate and is best described with reference to Fig. 3.

The basic hydrogen-bonded motif consists of two asymmetric units related by the centre of inversion at 0, $\frac{1}{2}$, $\frac{1}{2}$: within this basic structural unit there are two forms of disorder. The morpholine molecule and the water molecule are positionally disordered across the inversion centre: at the same time there is orientational disorder of the morpholine molecule, with each heteroatom site [labelled ON(71) and ON(74)] occupied by one-half of an oxygen atom and one-half of a nitrogen atom. Fig. 4 shows the disorder of the morpholine and the water components in adduct **4b**: the atoms C(72) and C(76*) are coincident, as are C(76) and C(72*), because of the inversion centre. Overall the morpholine ring adopts a chair conformation, but because of the extensive disorder it was not possible to make any meaningful metrical comparison of the morpholine here with free morpholine.

Within this motif the hydroxyl-hydrogen atoms of the diol component could be located from a difference map, but the hydrogen atoms of the water molecule and the morpholine NH group could not. The hydrogen atom bonded to O(1) of the ferrocenediol component is disordered equally over two sites, with one site directed towards O(2) and the other towards the water molecule at $1-x$, $1-y$, $1-z$. The hydrogen atom bonded to O(2) is disordered over these sites: one site, with occupancy 0.5, is directed towards O(1); one with occupancy 0.25 is directed towards the water molecule at *x*, *y*, *z*; and the third, also with occupancy 0.25, is directed towards the heteroatom ON(74) at $-x$, $1-y$, $1-z$.

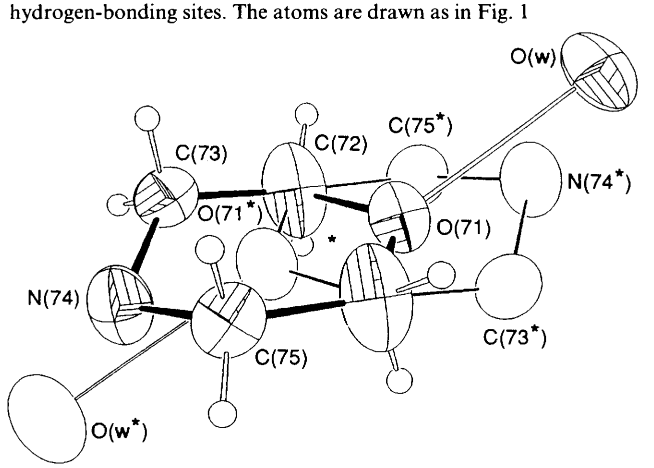

Fig. 4 View of the disordered morpholine and water components in adduct **4b**. For clarity, the atoms numbered 71 and 74 are labelled as oxygen and nitrogen respectively, although each such site is populated by 0.5(O + N): a common site is occupied by C(72) and C(76*)

This extensive arrangement of hydrogen bonds is doubtless augmented by further hydrogen bonds formed by the water molecule acting as a hydrogen-bond donor: the whole hydrogen-bonding network appears to be disordered, but may well involve mobile hydrogen atoms. The involvement of neighbouring motifs in adjacent unit cells in hydrogen bonds particularly that formed between O(1) and the water at $1-x$, $1-y$, $1-z$ means that examples of the basic motif discussed above are linked into ribbons parallel to the crystallographic *a* direction. In these ribbons the ferrocene units are on the outside, while the interior consists of the hydrogen-bonded system of ferrocene-based hydroxyl groups, and the water and morpholine molecules.

Dioxane adducts **5a** *and* **5b**. The dioxane adduct **5a** crystallises in the triclinic space group $P\bar{1}$: the structure contains a hydrogen-bonded aggregate (Fig. 5) comprising the diol molecules and a single dioxane molecule, lying across the centre of inversion at $\frac{1}{2}$, 0, $\frac{1}{2}$ together with an isolated dioxane molecule lying across the centre of inversion at 0, $\frac{1}{2}$, $\frac{1}{2}$. Within the hydrogen-bonded aggregate the diol forms both intra-

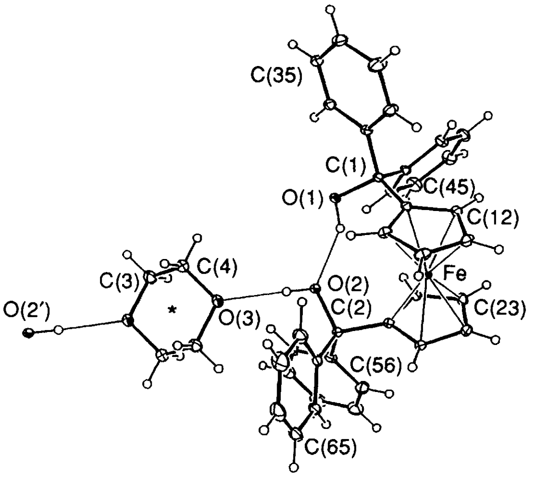

Fig. 5 View of the hydrogen-bonded aggregate in adduct **5a**, showing the atom-labelling scheme: the atoms are depicted as in Fig. 1. The non-bonded guest molecule, not shown, comprises the atoms O(4), C(5), C(6) and their symmetry-related counterparts

and inter-molecular O–H···O hydrogen bonds, with all the hydroxyl-hydrogen atoms ordered. The isolated dioxane molecule forms no hydrogen bonds of any kind but is trapped in a cavity: the structure of this phase thus resembles that of the 4,4′-bipyridyl adduct **2**. The centrosymmetry requires that both the independent dioxane molecules adopt the chair conformation. Fig. 10 shows a stereoview of the unit-cell contents.

Within the dioxane molecules the C–C and C–O distances found at 150 K for the hydrogen-bonded dioxane are 1.498(3) and 1.434(2) Å respectively, while for the trapped dioxane these dimensions are C–C 1.485(5) and C–O 1.405(4) and 1.426(4) Å (mean 1.415 Å). The C–C and C–O distances found[13] for gaseous 1,4-dioxane are 1.523(5) and 1.423(3) Å respectively: as for piperazine, the present C–C distances are somewhat less than those found by gas-phase electron diffraction while the mean C–X (X = O or N) distances are virtually the same as the gas-phase values.

The dioxane adduct **5b** crystallises in the monoclinic system with a host:guest ratio of 1:2. The diol component lies on a two-fold rotation axis with the dioxane guest in a general position. The diffraction data showed appreciable crystal decay, presumably due to loss of dioxane, and the refined structure showed a well defined diol component but with a highly disordered dioxane component with site occupancies less than unity, again due to progressive loss of dioxane during the data collection. It is noticeable that, at room temperature, crystals of the diol:dioxane adduct rapidly lose transparency when exposed to air, but that the crystal quality is readily restored by immersion of the crystals in dioxane. For this reason the crystals of the diol:dioxane adduct were stored under dioxane until required for X-ray investigation. In the structure of **5b** (Fig. 6) one only of the atoms of the disordered dioxane component is within hydrogen-bonding distance of the unique diol hydroxyl-hydrogen atom.

The unit-cell dimensions and space group of the adduct **5b** indicate that it is isomorphous and isostructural with the 1:2 diol:pyridine adduct the structure of which was reported earlier.[3] Since the pyridine molecule contains only a single hydrogen-bond acceptor site, whereas dioxane can in principle accept up to four hydrogen bonds, two at each oxygen, it is surprising to find such a similarity between the structures of the 1:2 adducts with pyridine[3] and dioxane. Fig. 11 shows a stereoview of the unit-cell contents for **5b**.

Dimethylformamide adduct **6**. In adduct **6** the hydrogen-bonded aggregate consists of one molecule each of the diol component **1** and dmf, forming a finite aggregate which contains three distinct types of hydrogen bond. Within the diol component there is an O–H···O hydrogen bond; there is an O–H···O intermolecular hydrogen bond between the two components and C–H···π (arene) hydrogen bond involving the unique formyl C–H bond of the dmf and two of the carbon atoms of the phenyl ring C(5*n*). The distances C(3)···C(52) and C(3)···C(51) are 3.524(4) and 3.616(4) Å respectively and H(3)···C(52) [with C(3)–H(3) set at 0.95 Å] is 2.73 Å; if the C(3)–H(3) distance is set at the more realistic value of 1.08 Å, then H(3)···C(52) becomes 2.64 Å. These values should be compared with O···C and (O)H···C distances of 3.525(4) and 2.73(4) Å found in 1,1,2-triphenylethanol,[14] where the O–H···π (arene) interactions are solely responsible for dimer formation. The hydrogen-bonded aggregate is shown in Fig. 7 and a stereoview of the unit-cell contents in Fig. 12. Within the Me_2NCHO component the dimensions are, within experimental uncertainty, identical to those observed[15] in the corresponding adduct with pyridine-2,5-dicarboxylic acid, except for the C–O distance: the value found here, 1.217(4) Å, is similar to the lower-quartile value for C=O in amides, while the value previously reported,[15] 1.273(5) Å, is longer than the upper-quartile value for any kind of C=O bond.[16]

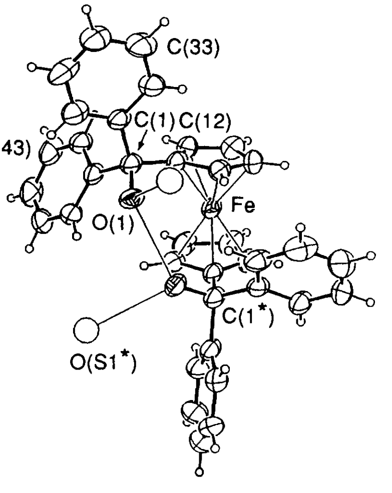

Fig. 6 View of the diol host component in adduct **5b**, showing the atom-labelling scheme and the guest-molecule atom, O(S), closest to the host component. The atoms are drawn as in Fig. 1

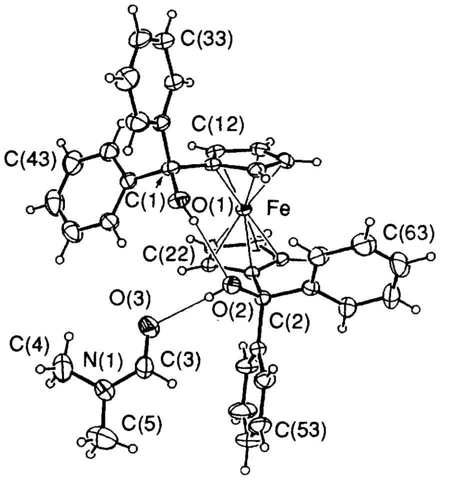

Fig. 7 View of the asymmetric unit in adduct **6**, showing the atom-labelling scheme. The atoms are depicted as in Fig. 2

The Structures and Conformations of the Diol Component in Adducts **2**–**6**.—The important dimensions of the diol host component in the adducts **2**–**6** are given in Table 2. The individual C–C distances in the cyclopentadienyl rings range

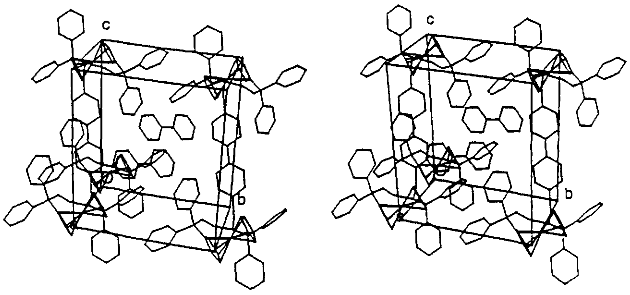

Fig. 8 Stereoview of the unit-cell contents of adduct **2**

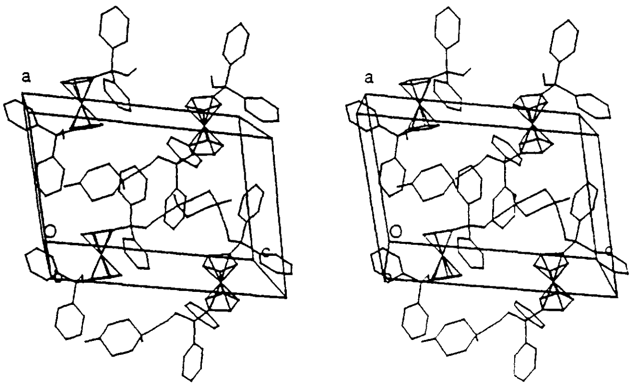

Fig. 9 Stereoview of the unit-cell contents of adduct **3**

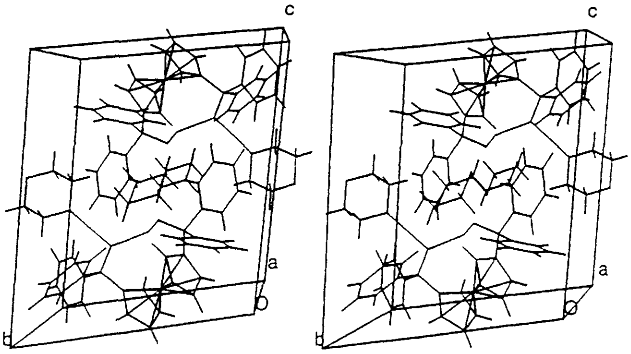

Fig. 10 Stereoview of the unit-cell contents of adduct **5a**

from a minimum of 1.400(4) Å in **6** to a maximum of 1.435(5) Å in **3**, with ranges running from 0.015 Å in **5a** to 0.033 Å in **3**: however the mean values for individual adducts are closely similar, with extremes of 1.417 Å in **6** (and in the pyridine adduct reported earlier[3]) and 1.426 Å in **5a**. The C–O bond lengths range from 1.416(2) Å in **4b** to 1.435(2) Å in **2**; these values may be compared with those in the methanol adduct[3] [1.440(3) and 1.431(3) Å] and the pyridine adduct[3] [1.424(2) Å]. The bond lengths involving the phenyl rings are unexceptional.

There are two conformational variables of importance: the relative twist of the cyclopentadienyl rings, and the conformation about the C–C bond exocyclic to the cyclopentadienyl rings. In each of the adducts **2**–**6** the atom-numbering scheme is such that C(1) is bonded to C(11) of the first cyclopentadienyl ring and C(2) is bonded to C(21) of the second ring. Hence a convenient measure of the relative twist of the rings is the torsion angle C(11)–Cp 1–Cp 2–C(21), where Cp 1 and Cp 2 represent the sites of the ring centroids: to allow for the fact that the rings do not have local C_5 rotational symmetry because of the variations in the ring C–C bond distances, the mean value of the torsion angles of C(1*n*)–Cp 1–Cp 2–C(2*n*) (for n = 1–5) is quoted in Table 2(*b*). For perfect eclipsing of the rings, this mean value should be $(72 \times n)°$ [for n = zero, or an integer, where $n = 0$ signifies eclipsing of the C(11)–C(1) and C(21)–C(2) bonds]. In all the adducts, except for that of piperazine **3**, the value of the mean twist angle is close to −72°, indicative of nearly eclipsed rings, with the exocyclic C–C bonds offset by one-fifth of a turn: this conformation is found also in the parent diol **1**[2] and in its adducts with pyridine and methanol.[3] On the other hand, in adduct **3** this mean twist angle is almost −180°, indicating nearly staggered rings with the exocyclic C–C bonds offset by one-half of a turn, so giving an almost locally centrosymmetric ferrocene skeleton in the diol component. This difference in conformation is clearly associated with the formation of an infinite chain structure in **3**, but of local, finite hydrogen-bonded aggregates in the other adducts, and in the parent diol.[2]

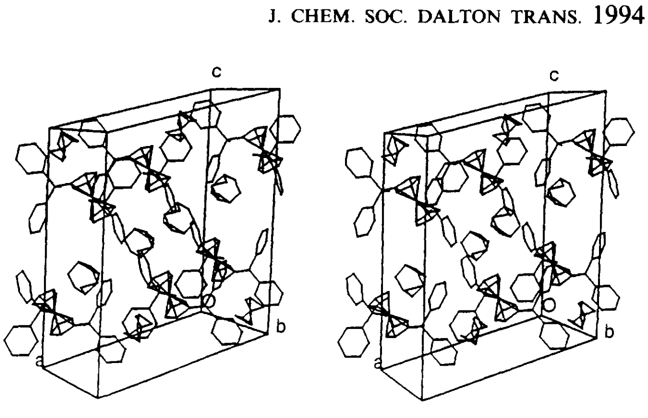

Fig. 11 Stereoview of the unit-cell contents of adduct **5b**

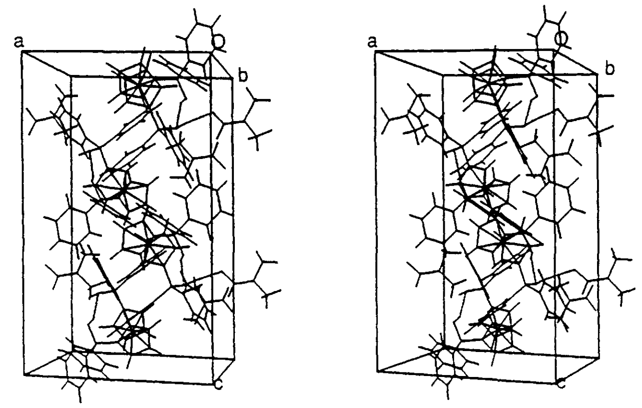

Fig. 12 Stereoview of the unit-cell contents of adduct **6**

The second important conformational variable is that around the exocyclic C–C bonds. Two generalisations can be made from the data in Table 2(*b*). First, despite the difference in the ring-twist angle observed for adduct **3**, the conformations about the exocyclic C–C bonds are broadly similar for all the adducts. Secondly, where there are two independent $C_5H_4CPh_2OH$ fragments (all adducts here except **5b**), the ferrocenediol component in each adduct has approximately two-fold rotational symmetry, whereas in **5b** the diol component has crystallographic two-fold symmetry. In like manner, both the parent diol **1** and the pyridine adduct have crystallographically imposed two-fold rotational symmetry,[2,3] while the methanol adduct also shows approximate two-fold symmetry for the case of the ferrocenediol component.

Hydrogen-bond Patterns in Diol **1** *and Its Adducts*.—The hydrogen-bond patterns in the ferrocenediol **1** and its adducts with 4,4′-bipyridyl **2**, piperazine **3**, 1,4-dioxane **5**, dimethylformamide **6**, methanol [3] and pyridine[3] can be analysed and codified in terms of graph sets, using rules set out by Etter and co-workers,[17,18] which have proven to be of great value in the description and analysis of hydrogen-bonding patterns in the crystal structure of sulfonamides and related compounds.[19] This analysis serves to emphasise the structural points in

Table 2 Selected dimensions (distances in Å, angles in °) for adducts **2**–**6**

(*a*) Bond lengths in host component	**2**	**3**	**4b**	**5a**	**5b**	**6**
C(11)–C(12)	1.421(3)	1.432(4)	1.430(2)	1.431(2)	1.415(15)	1.422(3)
C(12)–C(13)	1.426(3)	1.405(5)	1.424(2)	1.425(3)	1.396(14)	1.412(4)
C(13)–C(14)	1.403(3)	1.422(8)	1.421(3)	1.416(3)	1.446(16)	1.400(4)
C(14)–C(15)	1.420(3)	1.417(5)	1.422(3)	1.424(2)	1.374(17)	1.421(4)
C(15)–C(11)	1.429(2)	1.435(5)	1.425(2)	1.424(2)	1.424(11)	1.424(3)
Fe–Cp 1	1.6521(3)	1.6471(5)	1.6482(2)	1.6492(3)	1.648	1.6546(4)
C(21)–C(22)	1.429(2)	1.422(5)	1.432(2)	1.431(2)		1.424(3)
C(22)–C(23)	1.425(3)	1.405(7)	1.425(2)	1.429(2)		1.417(3)
C(23)–C(24)	1.411(3)	1.402(7)	1.405(3)	1.421(3)		1.411(4)
C(24)–C(25)	1.417(3)	1.418(5)	1.429(2)	1.431(2)		1.416(3)
C(25)–C(21)	1.429(2)	1.427(6)	1.427(2)	1.429(2)		1.422(3)
Fe–Cp 2	1.6470(3)	1.6483(5)	1.6525(2)	1.6513(3)		1.6512(4)
C(1)–C(11)	1.516(2)	1.517(4)	1.521(2)	1.518(2)	1.513(13)	1.517(3)
C(1)–O(1)	1.432(2)	1.430(3)	1.429(2)	1.426(2)	1.415(11)	1.432(3)
C(1)–C(31)	1.535(2)	1.537(4)	1.543(2)	1.532(2)	1.543(12)	1.541(3)
C(1)–C(41)	1.535(2)	1.532(5)	1.539(2)	1.532(2)	1.525(10)	1.535(3)
C(2)–C(21)	1.517(3)	1.524(5)	1.512(2)	1.516(2)		1.517(3)
C(2)–O(2)	1.435(2)	1.430(4)	1.416(2)	1.433(2)		1.434(3)
C(2)–C(51)	1.542(2)	1.545(4)	1.543(2)	1.537(2)		1.541(3)
C(2)–C(61)	1.534(2)	1.536(4)	1.536(2)	1.532(2)		1.525(3)
(*b*) Torsional angles in host component						
C(1*n*)–Cp 1–Cp 2–C(2*n*) (mean value)	−75.8	−171.3	−64.3	−64.9	−69.3*	−70.5
O(1)–C(1)–C(11)–C(12)	135.2(2)	169.1(3)	155.5(1)	151.7(2)	152.0(10)	155.3(3)
C(31)–C(1)–C(11)–C(12)	−106.2(2)	−73.8(2)	−87.6(1)	−93.1(1)	−91.4(8)	−89.4(2)
C(41)–C(1)–C(11)–C(12)	14.7(1)	49.3(2)	34.5(1)	28.5(1)	31.4(5)	31.9(1)
O(2)–C(2)–C(21)–C(22)	−37.9(1)	−24.0(2)	−44.0(1)	−54.2(1)		−41.7(1)
C(51)–C(2)–C(21)–C(22)	81.6(2)	94.9(3)	73.3(1)	63.2(1)		78.4(2)
C(61)–C(2)–C(21)–C(22)	−156.1(2)	−143.1(4)	−166.8(1)	−173.4(2)		−159.6(3)

(*c*) Hydrogen-bond distances

2 O(1) $\cdots$ O(2) 2.948(2), O(2) $\cdots$ N(71) 2.799(2); **3** O(1) $\cdots$ N(71) 2.821(3), O(2) $\cdots$ N(74$^{\text{II}}$) 2.867(3)
4b O(1) $\cdots$ O(2) 2.748(2), O(2) $\cdots$ O(w) 2.748(4), O(w) $\cdots$ ON(71) 2.634(5), O(1) $\cdots$ O(w$^{\text{III}}$) 2.631(4), O(2) $\cdots$ ON(74$^{\text{IV}}$) 2.840(4)
5a O(1) $\cdots$ O(2) 2.759(2), O(2) $\cdots$ O(3) 2.840(3); **5b** O(1) $\cdots$ O(1$^{\text{I}}$) 2.849(11), O(1) $\cdots$ O(S1) 2.93(2)
6 O(1) $\cdots$ O(2) 2.979(2), O(2) $\cdots$ O(3) 2.721(3), C(3) $\cdots$ C(51) 3.616(4), C(3) $\cdots$ C(52) 3.524(4)

(*d*) Bond lengths in guest components

Adduct **2**							
N(71)–C(72)	1.318(3)	C(75)–C(76)	1.385(3)	N(81)–C(82)	1.297(6)	C(85)–C(86)	1.363(5)
C(72)–C(73)	1.382(3)	C(76)–N(71)	1.325(3)	C(82)–C(83)	1.379(6)	C(86)–N(81)	1.300(6)
C(73)–C(74)	1.385(3)	C(74)–C(74$^{\text{V}}$)	1.490(3)	C(83)–C(84)	1.382(5)	C(84)–C(84$^{\text{VI}}$)	1.471(5)
C(74)–C(75)	1.380(3)			C(84)–C(85)	1.385(4)		
Adduct **3**							
N(71)–C(72)	1.454(5)	C(73)–N(74)	1.450(6)	N(74)–C(75)	1.458(6)	C(76)–N(71)	1.476(7)
C(72)–C(73)	1.505(6)			C(75)–C(76)	1.487(6)		
Adduct **4b**							
ON(71)–C(72)	1.483(5)	ON(74)–C(75)	1.491(6)	ON(71)–ON(71$^{\text{IV}}$)	1.388(7)	ON(71)–ON(74$^{\text{IV}}$)	1.552(5)
C(72)–C(73)	1.409(6)	C(75)–C(76)	1.464(8)	ON(71)–C(73$^{\text{IV}}$)	1.279(6)	ON(71)–C(75$^{\text{IV}}$)	1.715(6)
C(73)–ON(74)	1.478(6)	C(76)–ON(71)	1.224(9)				
Adduct **5a**							
O(3)–C(4)	1.434(2)	C(3)–O(3$^{\text{VII}}$)	1.434(2)	O(4)–C(5)	1.405(4)	C(5)–C(6$^{\text{IV}}$)	1.485(5)
C(3)–C(4)	1.498(3)			O(4)–C(6)	1.426(4)		
Adduct **6**							
C(3)–O(3)	1.217(4)	C(3)–N(1)	1.311(4)	N(1)–C(4)	1.431(5)	N(1)–C(5)	1.438(5)

Symmetry positions: I $-x, y, \frac{1}{2} - z$; II $-x, -\frac{1}{2} + y, 1 - z$; III $1 - x, 1 - y, 1 - z$; IV $-x, 1 - y, 1 - z$; V $-1 - x, -y, 1 - z$; VI $2 - x, 1 - y, 1 - z$; VII $1 - x, 2 - y, 1 - z$.

* C(1*n*)–Cp 1–Cp 1$^{\text{I}}$–C(1*n*$^{\text{I}}$).

common between all these structures except for that of **3**: no such analysis has been undertaken for the morpholine adduct **4** because of the extensive disorder in the structure.

The parent ferrocenediol **1** crystallises as hydrogen-bonded dimers[2] in which the hydroxyl-hydrogen atoms all appear from X-ray analysis to be disordered over two equally populated sites. Use of ^{2}H magic angle spinning (MAS) NMR spectroscopy shows[20] that the hydrogen atoms are in fact mobile between the alternative sites, so that the essential features of the hydrogen bonding can be represented by **Ia** $\rightleftharpoons$ **Ib** (Scheme 1). Within the dimeric arrays **Ia** and **Ib** there are two types of hydrogen bond, intermolecular with graph-set descriptor[17,18,*] **D** and intramolecular with the descriptor S(8), where the

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* Hydrogen-bonded motifs and networks can be described and codified using pattern designators[17,18] of the general type $\mathbf{G}^a_d(r)$. 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.

Table 3 Summary of data collection, structure solution and refinement details

	2	**3**	**4b**	**5a**	**5b**	**6**
(*a*) Crystal data						
Mnemonic	**1**:0.5bipy:0.5bipy	**1**:pipz	**1**:0.5H_2O:0.5morph	**1**:0.5diox:0.5diox	**1**:2diox	**1**:dmf
Empirical formula	$C_{46}H_{38}FeN_2O_2$	$C_{40}H_{40}FeN_2O_2$	$C_{38}H_{35.5}FeH_{0.5}O_3$	$C_{40}H_{38}FeO_4$	$C_{44}H_{46}FeO_6$	$C_{39}H_{37}FeNO_3$
Structural formula	$C_{36}H_{30}FeO_2{\cdot}0.5C_{10}H_8N_2{\cdot}0.5C_{10}H_8N_2$	$C_{36}H_{30}FeO_2{\cdot}C_4H_{10}N_2$	$C_{36}H_{30}FeO_2{\cdot}0.5H_2O{\cdot}0.5C_4H_9NO$	$C_{36}H_{30}FeO_2{\cdot}0.5C_4H_8O_2{\cdot}0.5C_4H_8O_2$	$C_{36}H_{30}FeO_2{\cdot}2C_4H_8O_2$	$C_{36}H_{30}FeO_2{\cdot}C_3H_7NO$
M	706.67	636.61	603.05	638.59	774.74	623.57
Colour, habit	Pale yellow, plate	Yellow, plate	Yellow, block	Orange, block	Orange, cube	Pale yellow, block
Crystal size/mm	0.19 × 0.56 × 0.60	0.14 × 0.33 × 0.58	0.21 × 0.37 × 0.45	0.17 × 0.22 × 0.28	0.19 × 0.20 × 0.21	0.15 × 0.21 × 0.39
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
a/Å	9.703(1)	10.960(2)	8.751(1)	10.349(1)	16.450(1)	11.858(1)
b/Å	12.314(1)	9.531(1)	12.446(1)	11.972(1)	11.173(1)	13.369(2)
c/Å	15.722(1)	15.788(2)	15.323(1)	14.069(1)	21.026(1)	20.328(2)
α/°	86.89(1)	90	108.78(1)	98.43(1)	90	90
β/°	75.61(1)	104.06(1)	98.38(1)	95.86(1)	103.87(1)	92.67(1)
γ/°	84.17(1)	90	100.33(1)	110.35(1)	90	90
U/Å^3	1809.3(3)	1599.7(4)	1516.9(2)	1594.5(2)	3751.8(4)	3219.0(7)
Space group	$P\bar{1}$	$P2_1$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$
Z	2	2	2	2	4	4
Molecular symmetry	bipy molecules on inversion centres	None	Water and morph disordered	diox molecules on inversion centres	**1** on two-fold axis, diox disordered	None
F(000)	740	672	634	672	1536	1312
D_c/g cm^{-3}	1.297	1.322	1.320	1.330	1.372	1.287
μ/mm^{-1}	0.45	0.51	0.53	0.51	0.45	0.50
(*b*) Data acquisition[a]						
T/°C	21	21	21	−123	21	21
Unit cell reflections (2θ range/°)	25 (31–50)	25 (32–44)	25 (39–52)	44 (10–26)	25 (20–29)	25 (18–39)
Maximum 2θ/° for reflections	59.8	59.8	67.8	59.9	53.8	53.8
Variation in 3 standard reflections (%)	± 1	< 1	± 1	10.6	> 25	< 1
Reflections measured	10 455	5091	12 324	9263	3627	7306
Unique reflections	10 455	4883	12 324	9263	3627	6984
R_{int}	—	0.013	—	—	—	0.012
Reflections with $I > n\sigma(I)$, n	6926, 3.0	3326, 3.0	8760, 3.0	6914, 3.0	2085, 2.5	4323, 3.0
Absorption correction type	9 ψ scans	9 ψ scans	9 ψ scans	9 ψ scans	None	9 ψ scans
Minimum, maximum absorption correction	0.7520, 0.8710	0.7360, 0.8738	0.7521, 0.7994	0.6551, 0.9656		0.8913, 0.9123
(*c*) Structure solution and refinement[b]						
H-Atom treatment (CH riding)	OH from Δ map	OH from Δ map	Some OH from Δ map	OH from Δ map		OH from Δ map
No. variables	460	405	415	406	186	398
k in $w = 1/(\sigma^2F_o + kF_o^2)$	0.0008	0.0008	0.0010	0.0008	0.0008	0.0008
R, R', S	0.038, 0.052, 1.41	0.032, 0.041, 1.10	0.043, 0.064, 1.57	0.038, 0.050, 1.18	0.111, 0.159, 4.01	0.035, 0.047, 1.18
Density range in final Δ map/e Å^{-3}	−0.46, 0.28	−0.23, 0.44	−0.29, 0.46	−0.36, 0.36	−0.78, 0.99	−0.23, 0.22
Final shift/error ratio	0.001	0.001	0.001	0.000	0.031	0.001

[a] Data collection on an Enraf–Nonius CAD4 diffractometer (except for **5a**, Siemens diffractometer) with graphite monochromatised Mo-Kα radiation (λ 0.710 67 Å). [b] All calculations were done on a Silicon Graphics 4D-35TG work station with the NRCVAX system of programs.[4] Solution method: Patterson heavy atom.

Table 4 Fractional coordinates

Atom	*x*	*y*	*z*
(*a*) Adduct **2**			
Fe	0.281 982(25)	0.124 384(19)	0.199 526(15)
Cp 1	0.395 996	0.024 152	0.151 306
Cp 2	0.173 438	0.226 990	0.247 486
O(1)	0.069 11(12)	−0.091 06(10)	0.221 95(9)
O(2)	−0.053 28(13)	0.108 88(9)	0.145 93(8)
C(1)	0.212 33(17)	−0.127 72(13)	0.225 71(11)
C(11)	0.312 85(17)	−0.041 26(13)	0.187 36(11)
C(12)	0.422 42(19)	−0.004 03(15)	0.220 78(13)
C(13)	0.494 62(19)	0.072 24(17)	0.158 06(14)
C(14)	0.430 82(21)	0.082 11(16)	0.086 82(13)
C(15)	0.319 27(20)	0.011 70(15)	0.103 51(11)
C(2)	−0.006 71(17)	0.216 59(13)	0.139 75(10)
C(21)	0.097 88(18)	0.220 42(13)	0.196 70(11)
C(22)	0.084 82(18)	0.165 27(14)	0.280 28(11)
C(23)	0.194 25(21)	0.195 18(17)	0.317 95(12)
C(24)	0.274 08(21)	0.269 10(17)	0.258 53(14)
C(25)	0.216 16(19)	0.284 98(14)	0.183 97(12)
C(31)	0.256 08(18)	−0.231 96(13)	0.172 57(11)
C(32)	0.395 85(20)	−0.260 36(15)	0.127 64(13)
C(33)	0.433 17(25)	−0.358 05(18)	0.083 82(16)
C(34)	0.330 60(27)	−0.427 43(18)	0.084 45(17)
C(35)	0.191 75(27)	−0.399 78(19)	0.128 76(19)
C(36)	0.153 76(21)	−0.302 61(17)	0.172 24(16)
C(41)	0.211 62(20)	−0.156 71(15)	0.322 03(11)
C(42)	0.321 73(25)	−0.221 52(20)	0.344 31(14)
C(43)	0.318 87(34)	−0.249 97(25)	0.431 97(18)
C(44)	0.203 51(38)	−0.212 82(28)	0.496 93(16)
C(45)	0.095 50(35)	−0.145 74(28)	0.475 55(16)
C(46)	0.098 61(26)	−0.117 78(21)	0.389 35(14)
C(51)	−0.138 73(18)	0.298 63(14)	0.170 33(11)
C(52)	−0.247 94(20)	0.302 61(16)	0.127 00(13)
C(53)	−0.371 50(22)	0.371 89(19)	0.154 12(16)
C(54)	−0.387 18(24)	0.437 92(18)	0.224 22(17)
C(55)	−0.280 26(26)	0.435 45(18)	0.266 94(16)
C(56)	−0.155 33(22)	0.365 99(16)	0.240 31(14)
C(61)	0.065 21(18)	0.240 40(15)	0.042 94(11)
C(62)	0.105 01(21)	0.157 30(17)	−0.016 50(12)
C(63)	0.179 49(26)	0.179 53(23)	−0.102 94(14)
C(64)	0.210 96(25)	0.284 61(26)	−0.129 44(14)
C(65)	0.167 50(23)	0.367 52(21)	−0.072 00(15)
C(66)	0.094 10(21)	0.346 10(16)	0.014 11(13)
N(71)	−0.273 04(17)	0.071 83(14)	0.294 85(10)
C(72)	−0.375 09(24)	0.141 63(17)	0.338 01(13)
C(73)	−0.467 15(21)	0.117 63(15)	0.417 66(12)
C(74)	−0.453 20(17)	0.014 78(14)	0.456 54(11)
C(75)	−0.349 25(23)	−0.059 46(17)	0.410 14(14)
C(76)	−0.262 75(22)	−0.027 82(18)	0.330 41(14)
N(81)	0.699 83(36)	0.658 45(25)	0.453 13(25)
C(82)	0.688 53(41)	0.594 03(34)	0.522 09(33)
C(83)	0.801 19(41)	0.530 77(29)	0.543 80(26)
C(84)	0.937 64(30)	0.532 85(19)	0.490 50(19)
C(85)	0.947 53(40)	0.602 17(32)	0.417 24(27)
C(86)	0.828 10(51)	0.660 81(34)	0.402 87(29)
(*b*) Adduct **3**			
Fe	−0.002 06(4)	0.25	0.253 81(3)
Cp 1	0.144 158	0.207 888	0.255 144
Cp 2	−0.148 238	0.292 502	0.252 660
O(1)	0.218 35(19)	0.284 34(26)	0.473 46(13)
O(2)	−0.224 62(23)	−0.036 17(30)	0.162 08(18)
C(1)	0.241 01(25)	0.363 52(33)	0.401 90(17)
C(11)	0.182 30(27)	0.279 79(37)	0.320 45(18)
C(12)	0.161 69(29)	0.324 39(41)	0.231 47(21)
C(13)	0.117 40(31)	0.210 03(45)	0.176 37(20)
C(14)	0.109 33(34)	0.091 57(46)	0.229 47(24)
C(15)	0.150 07(34)	0.133 66(43)	0.317 96(23)
C(2)	−0.247 44(29)	0.101 06(39)	0.125 05(20)
C(21)	−0.187 49(31)	0.206 66(41)	0.195 31(20)
C(22)	−0.161 61(33)	0.183 65(53)	0.286 94(22)
C(23)	−0.117 44(33)	0.309 28(53)	0.330 18(22)
C(24)	−0.116 02(33)	0.412 60(49)	0.267 20(25)
C(25)	−0.158 63(32)	0.350 32(45)	0.183 67(22)
C(31)	0.383 94(27)	0.376 09(37)	0.413 57(18)
C(32)	0.449 84(29)	0.288 45(41)	0.370 74(22)
C(33)	0.581 13(36)	0.295 30(49)	0.388 44(26)
C(34)	0.645 54(33)	0.388 74(54)	0.448 50(25)
C(35)	0.581 66(33)	0.478 99(50)	0.490 22(26)
C(36)	0.451 21(31)	0.472 86(45)	0.472 65(22)
C(41)	0.180 67(26)	0.509 10(36)	0.398 51(19)
C(42)	0.207 69(33)	0.612 97(38)	0.344 72(22)
C(43)	0.148 02(40)	0.742 49(52)	0.337 13(27)
C(44)	0.059 60(38)	0.768 12(48)	0.384 41(31)
C(45)	0.034 01(35)	0.668 51(51)	0.439 89(29)
C(46)	0.094 90(32)	0.538 33(44)	0.448 21(22)
C(51)	−0.390 87(29)	0.125 79(46)	0.095 49(20)
C(52)	−0.459 28(35)	0.048 67(49)	0.024 74(22)
C(53)	−0.588 03(35)	0.063 31(55)	−0.001 97(24)
C(54)	−0.650 85(35)	0.154 49(62)	0.039 39(28)
C(55)	−0.584 28(34)	0.230 61(66)	0.108 87(27)
C(56)	−0.454 32(32)	0.217 84(48)	0.136 75(23)
C(61)	−0.188 49(28)	0.112 00(39)	0.046 44(19)
C(62)	−0.103 14(36)	0.011 11(46)	0.033 54(24)
C(63)	−0.045 41(38)	0.024 92(61)	−0.034 67(27)
C(64)	−0.070 38(39)	0.138 12(65)	−0.090 24(25)
C(65)	−0.156 67(35)	0.235 71(61)	−0.079 01(21)
C(66)	−0.216 63(31)	0.222 83(44)	−0.011 04(21)
N(71)	0.391 99(30)	0.276 12(44)	0.637 76(18)
C(72)	0.307 64(41)	0.209 60(52)	0.683 93(24)
C(73)	0.371 73(49)	0.166 14(51)	0.775 59(26)
N(74)	0.431 14(32)	0.287 64(37)	0.823 73(19)
C(75)	0.524 39(37)	0.347 35(58)	0.782 12(28)
C(76)	0.461 22(41)	0.390 72(55)	0.691 61(27)
(*c*) Adduct **4b**[a]			
Fe	0.810 524(24)	0.563 671(16)	0.862 583(13)
Cp 1	0.910 706	0.481 056	0.798 392
Cp 2	0.718 494	0.647 908	0.932 664
O(1)	0.558 82(19)	0.395 69(10)	0.627 69(8)
C(1)	0.639 33(21)	0.332 91(12)	0.674 85(10)
C(11)	0.786 25(19)	0.416 45(12)	0.746 49(10)
C(12)	0.868 59(19)	0.406 22(13)	0.830 08(11)
C(13)	1.008 71(21)	0.498 90(15)	0.869 34(14)
C(14)	1.013 32(23)	0.567 18(15)	0.810 76(15)
C(15)	0.876 66(23)	0.516 53(14)	0.735 29(12)
O(2)	0.504 30(17)	0.611 23(10)	0.715 22(8)
C(2)	0.580 40(19)	0.714 48(12)	0.793 67(10)
C(21)	0.664 19(18)	0.676 66(12)	0.868 10(10)
C(22)	0.591 47(19)	0.579 77(13)	0.891 24(11)
C(23)	0.694 98(22)	0.578 02(16)	0.971 45(11)
C(24)	0.829 70(22)	0.671 62(16)	0.997 99(11)
C(25)	0.812 13(19)	0.733 47(13)	0.934 54(1)
C(42)	0.562 61(22)	0.189 43(14)	0.756 42(12)
C(43)	0.462 23(27)	0.137 42(17)	0.801 73(14)
C(44)	0.320 54(31)	0.168 15(22)	0.812 33(17)
C(45)	0.278 42(26)	0.247 27(23)	0.776 35(18)
C(46)	0.378 95(25)	0.301 29(18)	0.730 58(14)
C(51)	0.451 66(18)	0.775 31(13)	0.830 71(13)
C(52)	0.351 98(25)	0.806 91(21)	0.770 05(19)
C(53)	0.235 53(27)	0.863 04(24)	0.800 64(25)
C(54)	0.218 16(25)	0.889 89(19)	0.890 55(24)
C(55)	0.314 21(31)	0.859 03(23)	0.951 22(20)
C(56)	0.432 09(25)	0.801 88(19)	0.921 76(15)
C(61)	0.694 47(20)	0.800 82(14)	0.766 14(12)
C(62)	0.729 83(27)	0.770 62(21)	0.677 23(15)
C(63)	0.822 76(33)	0.853 13(30)	0.651 82(20)
C(64)	0.887 31(31)	0.964 51(28)	0.714 95(25)
C(65)	0.855 42(28)	0.995 77(19)	0.804 30(21)
C(66)	0.759 40(24)	0.914 70(16)	0.829 76(16)

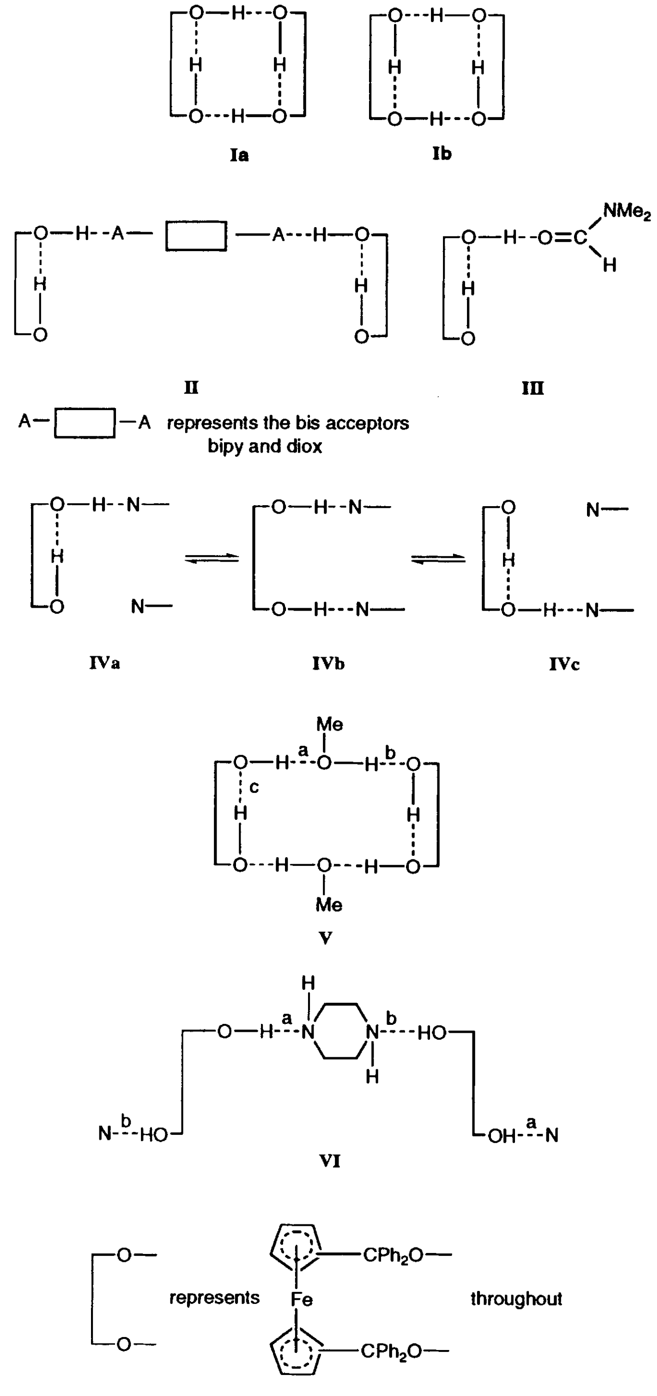
Table 4 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*c*) Adduct **4b**[a]							
C(31)	0.687 73(24)	0.238 39(13)	0.598 01(10)	O(w)	0.388 10(44)	0.575 61(40)	0.528 99(28)
C(32)	0.833 06(29)	0.213 30(17)	0.607 85(14)	ON(71)	0.076 63(42)	0.533 95(34)	0.508 96(28)
C(33)	0.868 99(38)	0.124 44(21)	0.536 25(17)	C(72)	0.022 12(40)	0.408 54(29)	0.495 20(26)
C(34)	0.752 15(41)	0.060 33(19)	0.453 97(17)	C(73)	−0.129 22(59)	0.360 20(37)	0.433 95(31)
C(35)	0.607 32(40)	0.085 63(18)	0.444 14(15)	ON(74)	−0.255 06(44)	0.425 53(31)	0.440 21(31)
C(36)	0.570 70(29)	0.172 72(16)	0.514 91(13)	C(75)	−0.183 00(60)	0.546 00(39)	0.445 26(33)
C(41)	0.523 45(20)	0.273 51(13)	0.721 49(11)	C(76)	−0.022 12	0.591 46	0.504 80
(*d*) Adduct **5a**							
Fe	0.192 268(24)	0.428 941(21)	0.115 512(16)	C(42)	0.413 35(19)	0.204 40(15)	0.245 00(13)
Cp 1	0.096 274	0.328 890	0.173 768	C(43)	0.517 36(21)	0.170 53(16)	0.209 43(14)
Cp 2	0.283 270	0.519 898	0.048 618	C(44)	0.643 65(21)	0.257 92(19)	0.202 11(16)
O(1)	0.374 60(13)	0.488 88(10)	0.361 15(8)	C(45)	0.665 33(21)	0.379 49(18)	0.230 93(16)
C(1)	0.319 29(17)	0.364 77(14)	0.312 50(12)	C(46)	0.561 47(19)	0.413 89(16)	0.267 12(14)
C(11)	0.199 17(17)	0.345 69(14)	0.232 60(11)	C(51)	0.495 38(18)	0.813 82(15)	0.166 10(12)
C(12)	0.150 00(18)	0.258 86(15)	0.142 97(12)	C(52)	0.601 57(19)	0.894 36(16)	0.240 10(14)
C(13)	0.026 89(19)	0.269 28(16)	0.096 51(13)	C(53)	0.720 86(20)	0.977 91(17)	0.217 86(16)
C(14)	0.000 03(18)	0.362 11(18)	0.156 17(13)	C(54)	0.736 71(21)	0.982 97(18)	0.122 39(18)
C(15)	0.105 28(17)	0.408 51(16)	0.240 59(12)	C(55)	0.632 47(24)	0.903 39(19)	0.047 94(16)
O(2)	0.397 45(13)	0.691 42(10)	0.282 30(8)	C(56)	0.513 50(21)	0.819 66(17)	0.069 89(14)
C(2)	0.362 91(17)	0.722 84(14)	0.191 17(11)	C(61)	0.247 05(18)	0.774 48(14)	0.197 26(12)
C(21)	0.313 29(17)	0.606 63(14)	0.115 14(11)	C(62)	0.149 27(22)	0.734 03(18)	0.257 66(15)
C(22)	0.391 08(17)	0.529 57(15)	0.098 40(12)	C(63)	0.042 58(26)	0.778 65(23)	0.264 36(18)
C(23)	0.319 55(20)	0.439 41(16)	0.012 94(13)	C(64)	0.031 26(25)	0.863 53(21)	0.210 40(18)
C(24)	0.198 34(20)	0.460 20(15)	−0.023 20(12)	C(65)	0.127 60(23)	0.903 87(18)	0.150 36(16)
C(25)	0.194 09(18)	0.563 68(15)	0.039 81(12)	C(66)	0.234 37(20)	0.859 69(16)	0.143 13(13)
C(31)	0.266 61(18)	0.292 27(14)	0.391 07(12)	C(3)	0.591 40(28)	1.004 00(20)	0.581 11(15)
C(32)	0.140 52(22)	0.195 04(18)	0.375 26(14)	C(4)	0.464 69(27)	0.893 29(19)	0.537 20(14)
C(33)	0.097 52(25)	0.132 84(21)	0.449 54(16)	O(3)	0.431 15(18)	0.888 11(13)	0.434 83(10)
C(34)	0.181 46(24)	0.167 37(18)	0.540 83(14)	O(4)	0.056 65(28)	0.580 60(19)	0.438 76(13)
C(35)	0.307 06(21)	0.263 56(16)	0.556 68(13)	C(5)	−0.078 82(35)	0.557 93(31)	0.460 04(22)
C(36)	0.350 07(19)	0.326 12(15)	0.483 08(12)	C(6)	0.142 23(34)	0.565 35(32)	0.518 11(24)
C(41)	0.434 04(17)	0.327 37(15)	0.273 24(12)				
(*e*) Adduct **5b**[b]							
Fe	0.0	0.196 1(2)	0.25	C(41)	−0.188 8(5)	0.386 4(9)	0.243 0(4)
Cp 1	−0.056 1	0.193 0	0.173 7	C(42)	−0.260 1(5)	0.314 4(10)	0.233 6(4)
O(1)	−0.081 5(3)	0.491 7(6)	0.207 2(3)	C(43)	−0.303 1(6)	0.297 4(11)	0.280 9(6)
C(1)	−0.139 5(5)	0.396 7(9)	0.190 3(4)	C(44)	−0.274 6(9)	0.359 5(15)	0.341 0(6)
C(11)	−0.093 4(5)	0.282 1(9)	0.183 3(4)	C(45)	−0.208 1(8)	0.427 8(13)	0.349 6(5)
C(12)	−0.115 2(5)	0.162 0(10)	0.192 9(5)	C(46)	−0.165 3(6)	0.449 0(9)	0.302 2(4)
C(13)	−0.056 8(6)	0.084 7(11)	0.176 4(5)	O(S1)	−0.022 0	0.618 1	0.105 0
C(14)	0.003 7(6)	0.159 5(12)	0.155 6(5)	C(S2)	−0.062 3	0.620 3	0.045 2
C(15)	−0.018 8(5)	0.277 0(11)	0.160 3(4)	C(S3)	−0.051 6	0.814 1	0.083 4
C(31)	−0.199 3(5)	0.433 1(9)	0.124 8(4)	C(S4)	0.008 3	0.786 3	0.018 8
C(32)	−0.198 3(6)	0.377 7(11)	0.065 8(5)	C(S5)	0.038 7	0.817 7	0.085 5
C(33)	−0.250 0(8)	0.414 9(13)	0.007 2(5)	C(S6)	0.000 1	0.730 0	0.128 3
C(34)	−0.304 6(7)	0.507 3(13)	0.008 0(5)	C(S7)	−0.026 7	0.685 4	0.002 4
C(35)	−0.305 4(6)	0.561 7(12)	0.063 1(6)	C(S8)	0.062 9	0.762 5	0.059 6
C(36)	−0.253 7(6)	0.525 3(10)	0.123 0(5)	C(S9)	0.058 3	0.657 2	0.055 6
(*f*) Adduct **6**							
Fe	0.402 100(27)	0.132 856(23)	0.091 125(16)	C(41)	0.152 40(21)	0.259 96(17)	0.003 50(13)
Cp 1	0.443 760	0.245 656	0.069 174	C(42)	0.168 58(25)	0.271 86(20)	−0.063 08(14)
Cp 2	0.364 980	0.017 662	0.109 884	C(43)	0.100 57(32)	0.223 98(26)	−0.110 28(16)
O(1)	0.178 05(15)	0.310 21(12)	0.118 80(8)	C(44)	0.014 29(33)	0.162 78(27)	−0.091 20(22)
O(2)	0.203 43(13)	0.149 42(12)	0.219 84(8)	C(45)	−0.002 97(28)	0.150 57(23)	−0.025 78(22)
C(1)	0.227 15(20)	0.314 28(17)	0.055 84(12)	C(46)	0.064 58(23)	0.199 03(20)	0.022 16(15)
C(11)	0.345 82(20)	0.271 95(15)	0.062 24(11)	C(51)	0.227 35(20)	−0.022 07(18)	0.257 20(12)
C(12)	0.412 19(21)	0.227 95(17)	0.013 45(11)	C(52)	0.174 33(24)	−0.011 94(22)	0.316 12(14)
C(13)	0.520 97(21)	0.208 62(18)	0.041 84(14)	C(53)	0.119 46(27)	−0.091 85(31)	0.343 21(17)
C(14)	0.523 76(22)	0.239 97(19)	0.107 58(14)	C(54)	0.116 68(34)	−0.182 81(32)	0.312 02(20)
C(15)	0.416 06(22)	0.279 79(16)	0.120 76(12)	C(55)	0.169 22(37)	−0.193 90(25)	0.254 50(19)
C(2)	0.284 79(18)	0.070 57(16)	0.228 48(11)	C(56)	0.224 97(28)	−0.113 99(20)	0.226 90(15)
C(21)	0.332 28(18)	0.046 11(15)	0.162 38(11)	C(61)	0.377 58(20)	0.108 02(17)	0.276 81(11)
C(22)	0.266 66(19)	0.039 64(16)	0.102 04(11)	C(62)	0.393 07(27)	0.209 01(20)	0.287 32(13)
C(23)	0.337 05(23)	0.002 81(17)	0.053 07(12)	C(63)	0.480 87(37)	0.243 05(27)	0.328 92(17)
C(24)	0.445 71(23)	−0.013 50(17)	0.082 31(12)	C(64)	0.552 41(33)	0.177 23(34)	0.360 54(16)
C(25)	0.443 20(19)	0.013 25(16)	0.149 62(11)	C(65)	0.537 72(27)	0.077 04(30)	0.351 17(16)
C(31)	0.231 80(21)	0.426 12(17)	0.037 75(12)	C(66)	0.450 39(24)	0.042 48(21)	0.309 77(14)
C(32)	0.316 79(23)	0.465 84(18)	0.001 74(14)	O(3)	−0.000 37(16)	0.080 61(17)	0.172 24(12)

Table 4 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*f*) Adduct **6**							
C(33)	0.316 14(27)	0.566 52(22)	−0.015 33(15)	N(1)	−0.168 79(20)	0.017 74(20)	0.197 76(13)
C(34)	0.231 81(32)	0.627 60(21)	0.004 17(18)	C(3)	−0.062 13(26)	0.039 68(24)	0.210 09(16)
C(35)	0.147 16(30)	0.589 34(23)	0.040 07(20)	C(4)	−0.221 29(31)	0.038 90(37)	0.134 49(21)
C(36)	0.146 71(26)	0.489 12(21)	0.057 08(17)	C(5)	−0.235 77(43)	−0.031 16(50)	0.245 44(28)

[a] The water and morpholine atoms O(w), ON(71), C(72), C(73), ON(74), C(75) and C(76) are present with 0.5 occupancy and are disordered about an inversion centre. Owing to the disorder, C(72) and C(76) occupy equivalent sites; coordinates for C(76) were obtained from those for C(72) by applying the transformation $-x$, $1 - y$, $1 - z$. Atoms ON(71) and ON(74) are disordered O and N atoms of the morpholine ring. [b] Atoms O(S1) to C(S9) are peaks found where the very disordered dioxane molecule would lie. No attempt was made to fit these peaks by a dioxane molecule as the crystal had decomposed during data collection.



Scheme 1 Hydrogen-bonding schemes in the ferrocene diol **1** and some of its adducts

smallest intramolecular ring is taken as eight-membered, thus: O–C–C (Cp)–Fe–C (Cp)–C–O–H. In terms of the priority rules for hydrogen bonds,[18] the intermolecular hydrogen bond has priority over the intramolecular bond, so that the graph-set assignment for the first-order network in this structure is N_1 = S(8)**D**. This assignment will recur in many of the adducts formed by the diol **1**. There is also a second-order network, N_2 = $\mathbf{R}^4_4(8)$, defining the central hydrogen-bonded ring in **I**.

Precisely the same graph sets, N_1 = S(8)**D**, N_2 = $\mathbf{R}^4_4(8)$, represent other ferrocenediols, regardless of whether the hydroxyl-hydrogen atoms are ordered as in racemic $[Fe(C_5H_4CH\,MeOH)_2]$[21] and $[Fe(C_5H_4CMe_2OH)_2]$[22] or disordered as in $[Fe(C_5H_4CPhMeOH)_2]$.[21] In contrast ferrocene monoalcohols have been observed to form both cyclic dimers, with graph set $\mathbf{R}^2_2(4)$ as in $[Fe(C_5H_5)(C_5H_4CPh_2OH)]$[2] and in $[\{Fe(C_5H_5)(C_5H_4)\}_2C(OH)CMe_3]$,[23] and linear chains as in racemic $[Fe(C_5H_4)CHPhOH]$[24] where each enantiomer occurs in two conformations giving the graph set N_1 = **DDDD**, N_2 = $\mathbf{C}^4_4(8)$.

The hydrogen bonding in both adducts **2** and **5a** can be represented by **II**: as for **I** there are two types of hydrogen bond, and the graph-set assignment is again S(8)**D**. Similarly, in the dimethylformamide adduct **6** the hydrogen-bonding can, apart from the C–H ··· π (arene) interaction, be represented as **III**, once again with graph set S(8)**D**. Hydrogen-bonding motifs of type **D** are typical of dimethylformamide adducts:[15,25] however in the 1:2 adduct with 1,1′-binaphthyl-2,2′-dicarboxylic acid[26] one molecule of dmf is hydrogen bonded to one of the carboxylic acid groups with an O–H ··· O bond of type **D**, but the other molecule uses both the formyl oxygen as hydrogen-bond acceptor from the carboxylic acid and the formyl hydrogen as hydrogen-bond donor to the acid, giving a cyclic array with graph set $\mathbf{R}^2_2(7)$.

In the 1:2 pyridine adduct of the ferrocenediol **1**[3] the hydroxyl-hydrogen atoms again appear to be disordered by X-ray analysis, but a plausible model of the hydrogen bonding involves rapid mobility of these hydrogen atoms, as found for the diol itself.[20] The hydrogen bonding can then be represented by **IVa** $\rightleftharpoons$ **IVb** $\rightleftharpoons$ **IVc**. In the tautomer **IVb**, in which both pyridine molecules are simultaneously hydrogen bonded to the diol, there is a single type of hydrogen bond, designated **D**. However in each of **IVa** and **IVc** there are both inter- and intramolecular hydrogen bonds, giving the now-familiar graph-set designation S(8)**D**. The 1:2 adduct with dioxane **5b** can probably be represented by a pattern analogous to **IVb** with graph set **D**.

In the 1:1 methanol adduct[3] the structure consists of a cyclic array formed of two molecules each of the ferrocenediol and of methanol: the hydrogen bonding can be symbolised as in **V** which indicates that there are three types of hydrogen bonds within the array. The hydrogen bonds denoted a and b are intermolecular, each designated **D**, of which a takes priority[18] as having the shorter O ··· O distance.[3] The hydrogen bond denoted c is intramolecular, giving the first-order network $N_1 = \mathbf{S}(8)\mathbf{DD}$. There is also a second-order network, $N_2 = \mathbf{R}_6^6(12)$, defining the central $(OH)_6$ ring in **V**.

In contrast to the finite adducts **2** and **4–6** and those formed by both pyridine and methanol, the piperazine adduct **3** is characterised by infinite-chain formation. The hydrogen-bonding scheme, symbolised as in **VI**, contains two distinct types of hydrogen bond, one involving an axial and the other an equatorial lone pair: each of these has the graph-set designator **D**, while the overall repeat pattern is a chain of length 13, so that $N_1 = \mathbf{DD}$ and $N_2 = \mathbf{C}_2^2(13)$.

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