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Hydrogen-bonded adducts of ferrocene-1,1′-diylbis(diphenylmethanol): a finite cyclic 1:1 adduct with 2,2′-dipyridylamine

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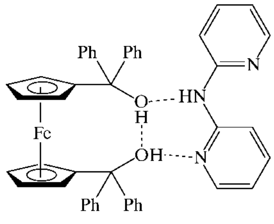
In ferrocene-1,1′-diylbis(diphenylmethanol)–2,2′-dipyridylamine (1/1), $[Fe(C_{18}H_{15}O)_2]\cdot C_{10}H_9N_3$, (I), there is an intramolecular O—H⋯O hydrogen bond [H⋯O 2.03 Å, O⋯O 2.775 (2) Å and O—H⋯O 147°] in the ferrocenediol component, and the two neutral molecular components are linked by one O—H⋯N hydrogen bond [H⋯N 1.96 Å, O⋯N 2.755 (2) Å and O—H⋯N, 157°] and one N—H⋯O hydrogen bond [H⋯O 2.26 Å, N⋯O 3.112 (2) Å and N—H⋯O 164°] forming a cyclic $R_3^3(8)$ motif. One of the pyridyl N atoms plays no part in the intermolecular hydrogen bonding, but participates in a short intramolecular C—H⋯N contact [H⋯N 2.31 Å, C⋯N 2.922 (2) Å and C—H⋯N 122°].

Comment

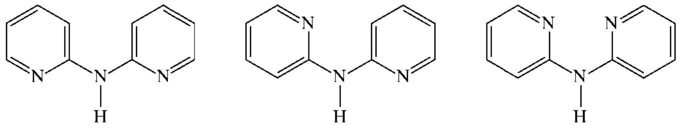
Ferrocene-1,1′-diylbis(diphenylmethanol), $[Fe(C_5H_4CPh_2\text{-}OH)_2]$, forms hydrogen-bonded adducts with a wide range of amines, particularly heteroaromatic amines and diamines. Thus with pyridine, this diol forms an adduct of stoichiometry (diol)·(amine)$_2$ (Ferguson *et al.*, 1993), in which the number of hydrogen-bond-donor hydroxyl groups is equal to the number of amine N acceptors: despite this, the molecular aggregate contains disordered O—H⋯O and O—H⋯N hydrogen bonds indicative of mobile hydroxyl H atoms.

Similarly, in the 1:1 adduct formed by the diol with 4,4′-bipyridyl (Glidewell *et al.*, 1994), the number of hydroxyl groups is equal to the number of N atoms but only half of the bipyridyl molecules are involved in the supramolecular aggregation, which takes the form of the centrosymmetric three-component aggregate diol–diamine–diol, while the remainder of the bipyridyl molecules simply occupy isolated sites in the structure (Glidewell *et al.*, 1994). By contrast, in each of the similar 1:1 adducts formed with 1,2-bis(4′-pyridyl)ethane (Zakaria *et al.*, 2001) and 1,2-bis(4′-pyridyl)-ethene (Zakaria *et al.*, 2002), there is a finite two-component aggregate containing one intramolecular O—H⋯O hydrogen bond and one intermolecular O—H⋯N hydrogen bond, while the second N atom plays no part in the hydrogen bonding. Continuing this theme, we have now synthesized and characterized a 1:1 adduct, (I), formed between the ferrocenediol and 2,2′-dipyridylamine, which was selected in order to increase the ratio of hydrogen-bond donors to acceptors in the expectation of forcing both pyridyl N atoms to participate in the supramolecular aggregation.



(I)

Compound (I) forms a finite 1:1 aggregate (Fig. 1) and, in addition to the intramolecular O—H⋯O hydrogen bond commonly found in adducts involving this diol (Ferguson *et al.*, 1993, 1995; Glidewell *et al.*, 1994; Zakaria *et al.*, 2001, 2002), there are two other hydrogen bonds, one each of the O—H⋯N and N—H⋯O types, linking the two molecular components by forming an $R_3^3(8)$ ring (Table 2, Fig. 1). It is striking that both of the hydroxyl O atoms act as both hydrogen-bond donors and acceptors, while pyridyl N3 forms no intermolecular hydrogen bonds. Moreover, the conformation of the nearly planar diamine (Table 1) is such that N2 is on the same edge of the diamine as the N11—H1 bond, while N3 is on the opposite edge. Atom N3 does, however, participate in a short intramolecular C—H⋯N contact (Table 2). In order to investigate whether this contact makes any significant contribution to the preferred conformation of the amine, we have undertaken SCF–MO calculations, using the *AM*1 technique (Dewar *et al.*, 1985; Stewart, 1990), for the three possible near-planar conformers (*A*)–(*C*) (see Scheme). Conformers (*A*) and (*C*) were both calculated to have C_2 symmetry, with N—C—N—C torsion angles of 155.0 and −24.3°, respectively, suggestive of repulsion between the *ortho*-C—H bonds in (*A*) and between the pyridyl N lone pairs in (*C*), and with enthalpies of formation respectively 1.5 and 2.2 kJ mol^{-1} higher than that of the planar conformer (*B*). Clearly these energy differences are insufficient to determine the overall conformation.



(*A*) (*B*) (*C*)

However, it is interesting to note that pure 2,2′-dipyridylamine crystallizes in three polymorphs: orthorhombic *Pccn*

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with $Z' = 1$ (Johnson & Jacobson, 1973), triclinic $P\overline{1}$ with $Z' = 2$ (Pyrka & Pinkerton, 1992) and monoclinic $P2_1/c$ with $Z' = 2$ (Schödel *et al.*, 1996), and that in each of these forms, the molecules adopt the same overall conformation as that observed here in (I). In the orthorhombic and triclinic forms, the molecules are linked into dimeric units by means of paired N—H···N hydrogen bonds, forming an $R_2^2(8)$ motif, with no involvement in the supramolecular aggregation of the N atom on the opposite edge of each molecule. On the other hand, in the monoclinic polymorph, where the molecules are linked into tetrameric aggregates, half of the molecules utilize all of their N atoms in the hydrogen bonding, acting as single donors and double acceptors, while the other half act as single donors only, leaving both pyridyl N atoms in these molecules uninvolved in the hydrogen bonding.

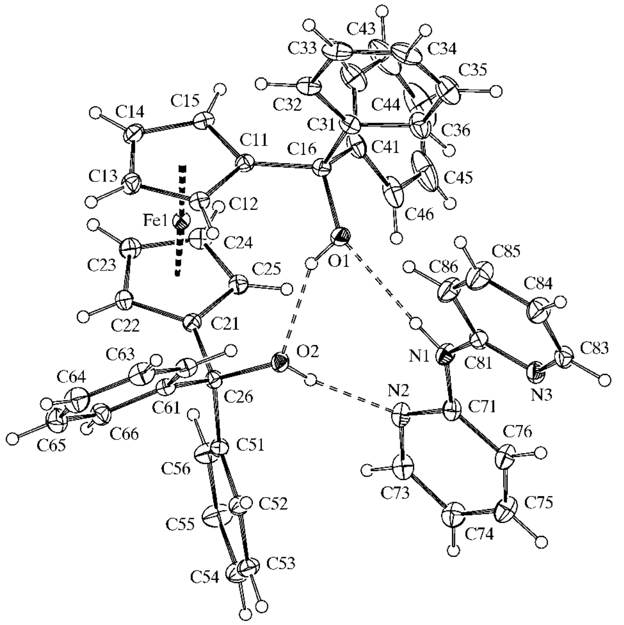

Figure 1
The molecular components of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

Equimolar quantities of the two components were separately dissolved in methanol; the solutions were mixed and the mixture was then set aside to crystallize, producing analytically pure (I). Analysis: found C 77.1, H 5.4, N 5.7%; $C_{46}H_{39}FeN_3O_2$ requires C 76.6, H 5.4, N 5.8%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$[Fe(C_{18}H_{15}O)_2]\cdot C_{10}H_9N_3$
$M_r = 721.65$
Monoclinic, $P2_1/c$
$a = 13.35070$ (10) Å
$b = 16.8198$ (2) Å
$c = 17.6306$ (2) Å
$\beta = 113.6410$ (7)°
$V = 3626.80$ (7) Å^3
$Z = 4$
$D_x = 1.322$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8310 reflections
$\theta = 2.7$–27.5°
$\mu = 0.46$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.35 × 0.32 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.856$, $T_{\max} = 0.874$
32 220 measured reflections
8294 independent reflections
7142 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 17$
$k = -21 \rightarrow 0$
$l = -22 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.095$
$S = 1.04$
8294 reflections
472 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 2.0419P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0049 (8)

Table 1
Selected torsion angles (°).

C81—N1—C71—N2	165.27 (15)	C71—N1—C81—N3	16.4 (2)
C81—N1—C71—C76	−14.2 (3)	C71—N1—C81—C86	−162.74 (17)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.84	2.03	2.7748 (15)	147
O2—H2···N2	0.84	1.96	2.7556 (17)	158
N1—H1*A*···O1	0.88	2.26	3.1116 (17)	164
C76—H76···N3	0.95	2.31	2.922 (2)	122

Compound (I) crystallized in the monoclinic system; space group $P2_1/c$ was uniquely assigned from the systematic absences. H atoms were treated as riding atoms with distances C—H = 0.95, N—H = 0.88 and O—H = 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1523). Services for accessing these data are described at the back of the journal.

References

Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3499–3506.

Ferguson, G., Glidewell, C., Lewis, A. & Zakaria, C. M. (1995). *J. Organometallic Chem.* **492**, 229–234.

Glidewell, C., Ferguson, G., Lough, A. J. & Zakaria, C. M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1971–1982.

Johnson, J. E. & Jacobson, R. A. (1973). *Acta Cryst.* B**29**, 1669–1674.

Nonius (1997). *KappaCCD Server Software.* Windows 3.11 Version. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.

Pyrka, G. J. & Pinkerton, A. A. (1992). *Acta Cryst.* C**48**, 91–94.

Schödel, H., Näther, C., Bock, H. & Butenschön, F. (1996). *Acta Cryst.* B**52**, 842–853.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Spek, A. L. (2001). *PLATON*. Version of October 2001. University of Utrecht, The Netherlands.

Stewart, J. J. P. (1990). *MOPAC*6.0. Quantum Chemistry Program Exchange, Bloomington, Indiana, USA.

Zakaria, C. M., Ferguson, G., Lough, A. J. & Glidewell, C. (2001). *Acta Cryst.* C**57**, 914–917.

Zakaria, C. M., Ferguson, G., Lough, A. J. & Glidewell, C. (2002). *Acta Cryst.* C**58**, m1–m4.