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High-symmetry inclusion compounds with mixed guests

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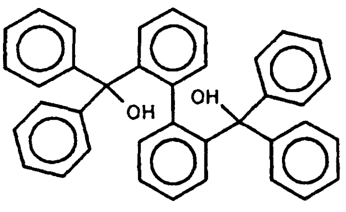
2,2′-Bis(hydroxydiphenylmethyl)-1,1′-biphenyl, H, forms two structurally similar inclusion compounds, $\mathrm{H{\cdot}H_2O{\cdot}\frac{1}{6}}$benzene (compound 1) and $\mathrm{H{\cdot}2\frac{1}{6}H_2O}$ (compound 2). In both crystal structures, six host molecules form a cyclomer linked *via* hydrogen bonding to bridging water molecules. In the case of compound 1 the resulting cavity encapsulates a benzene molecule, whereas compound 2 includes a total of $2\frac{1}{6}$ molecules of water per host to form an inclusion compound with an intricate H-bonding pattern.

Inclusion compounds, comprising a host and guest component, may be classified into two main groups: (*a*) molecular complexes, where the guest fits into the cavity of a host molecule, and (*b*) lattice clathrates, where the guest fits into the intermolecular spaces created by the packing of the host molecules.[1] In the latter case, it has been shown that host molecules should be rigid and bulky, in order to provide suitable cavities in the crystal structure which will accommodate a guest molecule.[2] In addition, it is often useful to incorporate a coordinating moiety in the host molecule, such as a hydrogen bonding donor or acceptor, which will enhance the process of molecular recognition between host and guest, and thus lead to the formation of the desired inclusion compound. This design strategy has recently been reviewed by Desiraju, who has coined the term 'supra molecular synthon', and has discussed its use in the process of crystal engineering.[3]

We have studied a number of host compounds based on the substituted 2,2′-biphenyl and binaphthyl host design, elucidated their structure and measured their thermal stabilities. We have shown that the inclusion compound formed between 2,2′-bis(hydroxydiphenylmethyl)-1,1′-binaphthyl and pyridine has a complex desolvation reaction in which the pyridine guest is emitted in two distinct steps which can be related to the host–pyridine bonding.[4] The structures formed between 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl and a variety of guests have been elucidated[5,6] and the activation energies of the desolvation reactions have been measured.[7] We have also determined the enthalpy of host–guest desolvation of the diethyl ether inclusion compound by accurate vapour pressure measurements.[8]

The compound **H** = 2,2′-bis(hydroxydiphenylmethyl)-1,1′-biphenyl has been synthesised by Toda *et al.*, who showed that it enclathrates a wide variety of guests, such as aliphatic alcohols, ketones, dioxane, carbon tetrachloride and dimethyl sulfoxide.[9] We report here the structures of the inclusion compounds $\mathrm{H{\cdot}H_2O{\cdot}\frac{1}{6}C_6H_6}$ (compound **1**) and $\mathrm{H{\cdot}2\frac{1}{6}H_2O}$ (compound **2**). Both inclusion compounds crystallise in the space group $R\bar{3}$.



H

Experimental

Single crystals of diffraction quality were obtained by slow evaporation of solutions of the host in wet benzene (compound **1**) or wet xylene (compound **2**). Although both inclusion compounds were remarkably stable, both crystals were sealed in Lindemann capillary tubes to protect the compounds from the atmosphere. X-Ray diffraction data were measured on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) with $\theta_{\max}$ = 25° ($\omega - 2\theta$ scans). Diffraction data for compound **1** were collected at room temperature (25 °C), but compound **2** was cooled to −100 °C using an Oxford Cryostream cooler in order to obtain better quality data. During the data collection, three reference reflections were monitored periodically to observe crystal stability. Refined unit cell parameters were obtained by least squares analysis of 24 reflections measured on the diffractometer in the range 16° < θ < 17°. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).†

Crystal data and other experimental details concerning the data collections and refinements are given in Table 1. ^{1}H NMR spectra were recorded using a Varian Unity FT-NMR spectrometer operating at 400 MHz. The host and inclusion compounds were dissolved in dry $\mathrm{CDCl_3}$ and ^{1}H NMR spectra were recorded at 25 °C. In all cases spectra were recorded with a sufficient pulse delay time to ensure quantitative resonance integrals to estimate host : guest ratios accurately. Thermogravimetry (TG) and differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer PC7 series system at a heating rate of 20° min^{-1}. The crystalline samples were removed from the mother liquor, blotted dry on filter paper and crushed. Sample weights were *ca.* 5 mg and dry nitrogen flowing at 40 cm^3 min^{-1} was used as a purge gas. Platinum sample pans with loose lids were used in the TG experiments and aluminium sample pans with crimped, but vented lids, were used for the DSC experiments.

Results and discussion

Nuclear magnetic resonance

The ^{1}H NMR spectrum of the pure host compared with that of inclusion compound **1** confirms the presence of benzene and water in the latter, with single sharp resonances at δ 7.36 and 1.56 assigned to benzene and $\mathrm{H_2O}$, respectively. Confirmation

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† For details of the CCDC deposition scheme, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1.

Table 1 Crystal data and refinement parameters

Compound	**1**	**2**
Molecular formula	$C_{38}H_{30}O_2 \cdot H_2O\frac{1}{6}C_6H_6$	$C_{38}H_{30}O_2 \cdot 2\frac{1}{6}H_2O$
M_r/g mol^{-1}	549.65	557.65
Crystal data		
Space group	$R\bar{3}$	$R\bar{3}$
a/Å	35.370(5)	35.123(2)
c/Å	12.570(8)	12.460(4)
Z	18	18
V/Å^3	13 619(9)	13 312(4)
D_c/g cm^{-3}	1.206	1.252
μ(Mo-Kα)/cm^{-1}	0.075	0.080
F(000)	5238	5322
Data collection		
Crystal dimensions/mm	0.38 × 0.38 × 0.30	0.38 × 0.44 × 0.44
Range scanned θ/degrees	1.15 to 24.97	1.16 to 24.98
Range of indices h,k,l	$-42 \leqslant h \leqslant 42, -42 \leqslant k \leqslant 42, 0 \leqslant l \leqslant 14$	$-41 \leqslant h \leqslant 0, 0 \leqslant k \leqslant 36, -14 \leqslant l \leqslant 14$
Reflections for lattice parameters no., θ range/degrees	24, 16–17	24, 16–17
Instability of standard reflections (%)	0.3	1.8
No. of unique reflections	5317	5199
No. of reflections observed with $I_{rel} > 2\sigma I_{rel}$	2587	3574
Final refinement		
No. of parameters	383	397
$R1$ ($I_{rel} > 2\sigma I_{rel}$)	0.0499	0.0432
$wR2$ ($I_{rel} > 2\sigma I_{rel}$)	0.1206	0.1104
Max. shift/esd	0.001	0.002
Max. height in electron density map/e Å^{-3}	0.426	0.405
Min. height in electron density map/e Å^{-3}	−0.245	−0.333

of the assignment of the δ 7.36 resonance to benzene was obtained by addition of a small quantity of benzene to a solution of the host. This resulted in a peak at δ 7.36 growing proportionately in intensity. The relative resonance integrals obtained from the spectrum supports formulation of the inclusion compound as $H \cdot H_2O \cdot \frac{1}{6}C_6H_6$ within experimental error. ^1H NMR experiments carried out on compound **2** confirmed the purity of the sample.

Thermal analysis

The thermal analytical results are shown in Fig. 1. The TG experiment on compound **1** [Fig. 1(*a*)] yields a satisfactory mass loss for the combined guests (calc. 5.7, found 6.8%). DSC yielded a single endotherm for the guest release reaction (peak A), followed by the melt of the host compound (peak B). Repeated attempts under various conditions of differing heating rates and crystalline size did not yield separate endotherms for the loss of benzene and water. A TG mass loss of 7.0% (calc. 6.97%) confirms the 1 : 2 $\frac{1}{6}$ host-to-guest stoichiometry for compound **2**. The thermal analytical traces [Fig. 1(*b*)] show that dehydration occurs in a diffuse step with an onset temperature of 70 °C.

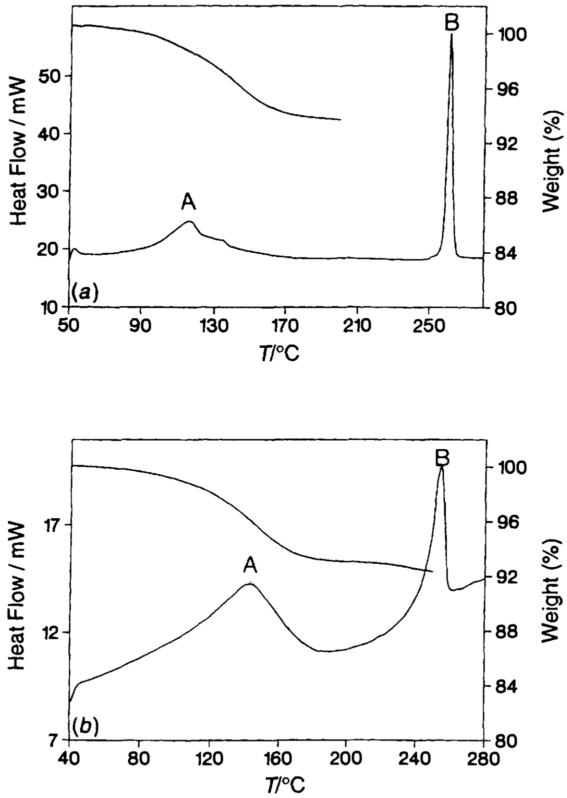

Fig. 1 TG and DSC curves for (*a*) compound **1** and (*b*) compound **2**

Structure solution and refinement

The crystal structure of compound **1** (based on hexagonal axes) was solved by direct methods, using the program SHELX-86.[10] The crystal structure of compound **2** was solved using the host heavy atom coordinates obtained from the structure solution of compound **1** in isomorphous replacement and the guest atoms were located in difference electron density maps. Both structures were refined on all F^2 values by full-matrix least-squares method using the program SHELXL.[11] The weighting scheme used is given in eqn. (1), where a and b are defined for

$$w = q/[\sigma^2(F_o^2) + (aP)^2 + (bP)] \qquad (1)$$

each structure and P = [0.333 33 × max of (O or F_o^2) + (1 − 0.333 33)F_c^2].

In both compounds the host molecule lies in a general position. Fig. 2 shows a perspective view of the host molecule, indicating the numbering scheme used. The conformation of the host is stabilised by an intramolecular hydrogen bond, O(7)–H(7) ··· O(26), which twists the two rings in the biphenyl moiety almost at right angles [C(14)–C(19)–C(20)–C(25) = 100°]. This is similar to the conformation found in the analogous compound 2,2′-bis(hydroxydiphenylmethyl)-1,1′-binaphthyl, whose crystal structure has been elucidated.[5] In both of our structures the host molecules are held by a series of

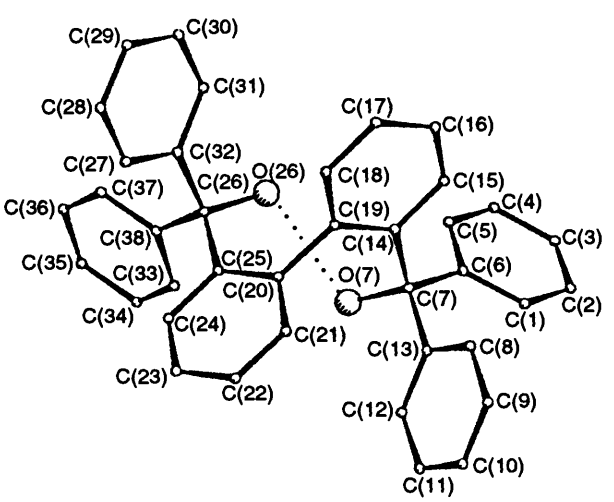

Fig. 2 Perspective view of the host molecule

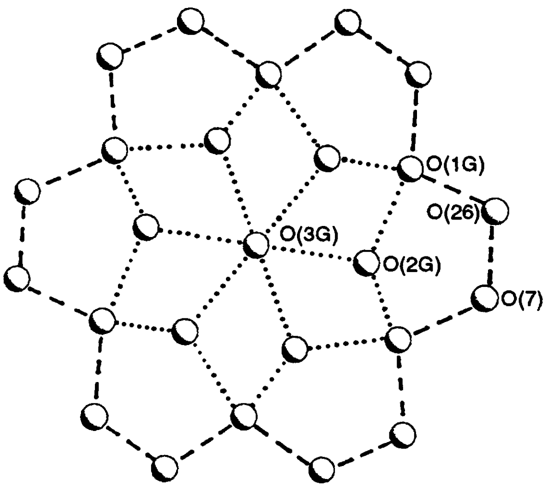

Fig. 3 Hydrogen bonding patterns observed (– – – in both structures; . . . in compound **2** only) as viewed down [001]

Table 2 H-bonding distances for compounds **1** and **2**

O···O	Compound	Distance/Å
O(7)···O(26)	1	2.724(3)
O(26)···O(1G)	1	2.795(3)
O(7)···O(1G)	1	2.828(3)
O(7)···O(26)	2	2.712(2)
O(26)···O(1G)	2	2.767(2)
O(7)···O(1G)	2	2.917(2)
O(1G)···O(2G)	2	2.799(3)
O(1G)···O(2G)	2	2.868(3)
O(2G)···O(3G)	2	3.043(5)

hydrogen bonds, involving bridging water molecules [O(1G)] and the hydroxy moieties of the host. The hydrogen-bonding patterns for compounds **1** and **2** are depicted in Fig. 3. The various hydrogen-bonding distances are shown in Table 2. The host molecules are locked into a hexagon by a ring of 18 hydrogen bonds, in which the pattern···O(7)···O(26)···O(1G)···O(7)··· is repeated six times by symmetry. This is similar to the packing arrangement of the inclusion compound of this host with acetone[9] in which the guest molecules are disordered.

For compound **1** the electron density map yielded the positions of all the host non-hydrogen atoms and a water molecule, and in addition a single peak at a distance of 1.4 Å from the origin at Wyckoff position (*a*). The $\bar{3}$ symmetry multiplies this to a regular hexagon with interatomic distances which refined to 1.411(7) Å. From TG and ^{1}H NMR spectra we interpret this as a benzene guest molecule. The benzene molecule fits deftly into the cavity formed by six phenyl rings, each from a different host molecule, in a $\bar{3}$ configuration, three above and three below the benzene molecule. Figs. 4 and 5 show how the benzene molecule fits into the cavity created by the host–water hydrogen-bonded arrangement. The structure was refined with anisotropic displacement parameters on the heavy atoms of the host and water molecules, but isotropically for the benzene molecule. Aromatic hydrogen atoms were constrained and refined as a riding model and hydroxy hydrogen atoms of the host were located in a difference electron density map and refined with a simple bond length constraint.[12] The hydrogen atoms of the water molecules were not located and were left out of the final model. The H-atoms on the benzene guest molecule were refined with temperature factors constrained at 120% that of the preceding C atom.

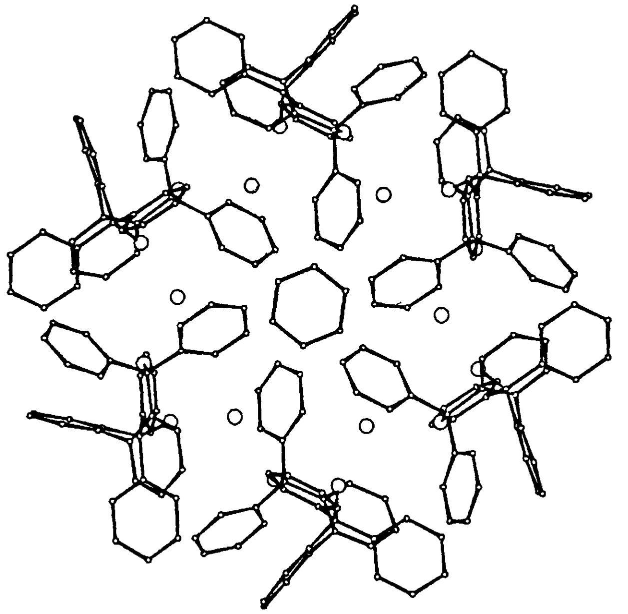

Fig. 4 Arrangement of six host molecules about the benzene guest molecule in compound **1** viewed down [001]

Fig. 5 Stereoscopic view of the arrangement of six host molecules about the benzene guest molecule (shown with van der Waals radii) in compound **1** viewed down [010]

In the structure refinement of compound **2** the electron density map yielded the positions of two water molecules [O(1G) and O(2G)] as well as a peak at (0,0,0.0386). Based on the TG results, this peak was interpreted as the O atom of a disordered water molecule with a site occupancy of 0.167. The structure was refined with anisotropic displacement parameters on the heavy atoms of the host molecule and on O(1G) and O(2G), but O(3G) was refined isotropically. Aromatic hydrogen atoms were constrained and refined as a riding model and hydroxy hydrogen atoms of the host, as well as the H-atoms on water molecule [O(1G)], were located in a difference electron density map and refined with a simple bond length constraint.[12] The hydrogen atoms of the remaining water molecules were not located and were left out of the final model.

As shown in Fig. 3, compound **2** exhibits additional H-bonding to the hydrogen bonded ring observed in both compounds. The pattern···O(2G)···O(1G)···O(2G)··· [with O(1G)···O(2G) = 2.799(3) and 2.868(3) Å, alternately] is repeated six times by the $\bar{3}$ axis to yield a star-shaped H-bonded ring. There is also evidence for a weak H-bond between

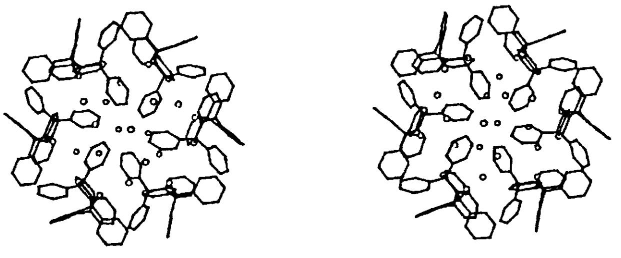

Fig. 6 Stereoscopic view of the arrangement of six host molecules about the water guest molecules in compound **2** as viewed down [001]

the O(2G) atoms related by the three-fold axis and O(3G) [O(2G)···O(3G) = 3.043 Å]. Fig. 6 shows a stereoscopic view of the the water oxygen atoms in compound **2** surrounded by six host molecules.

Compound **1** is a typical example of double molecular recognition, where the host molecules are assembled *via* hydrogen bonding to water, resulting in a cavity which encompasses the benzene guest. This is a somewhat different structure from that found in the 6:1 cyclohexanedione:benzene inclusion compound, in which the benzene guest fits precisely into the hexagonal cavity formed by six host molecules which are interlinked by hydrogen bonds.[13,14] In the case of compound **2** the same hydrogen-bonded assembly is observed, but the cavity is filled with another ring of hydrogen-bonded water molecules. The inclusion of both hydrophobic and hydrophylic guest molecules of suitable size therefore seems possible in this assembly.

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