Inclusion by a Novel Sexipedal Host. Crystal Structure and Thermal Analysis

Susan A. Bourne,[a] **Mino R. Caira,**[a] **Luigi R. Nassimbeni,**[a] **Muneyoshi Sakamoto,**[b] **Koichi Tanaka**[b] **and Fumio Toda***[,b]
[a] *Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa*
[b] *Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan*

Hexakis(3-hydroxy-3,3-diphenylpropynyl)benzene is a novel six-coordinate hydroxy host which enclathrates a variety of organic guests, including dimethylformamide.

The design of host molecules with specific enclathrating properties has received considerable attention and Weber has recently reviewed the principles of directed host design.[1] He has shown that a successful host molecule should be bulky and rigid in order to provide suitable cavities which can accommodate a guest species. In addition, it is often useful to add a functional group to the host molecule, which can engage in specific host–guest interactions. We have studied a number of inclusion compounds where the host molecule contains a hydroxy moiety as a hydrogen bonding donor, giving rise to 'coordinatoclathrates'.[2] Some of the most successful host molecules are of the 'wheel-and-axle' type which were first stynthesized by Toda.[3] The dynamics of enclathration of acetone by 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, as well as the solid–solid reaction of the same host with benzophenone have been studied.[4] The structures and thermal stabilities of a number of the inclusion compounds of the related host 4,4′-bis(diphenylhydroxymethyl)biphenyl have been determined.[5,6] The host: guest ratio in these compounds is generally 1:1 or 1:2, but in this work, the synthesis and structural elucidation of a new 'sexipedal' host, which enclathrates a variety of guests with variable host: guest ratios, is presented. Hexasubstituted benzene derivatives (the 'hexa-hosts') have been studied previously. Substituents were fairly flexible leading to some interesting inclusion behaviour.[7] The host described here however, contains rigid substituents with polar groups capable of hydrogen bonding which aid in the capture and stabilization of guest species.

We have synthesized hexakis(3-hydroxy-3,3-diphenylpropynyl)benzene, **1**, by the Pd-catalysed condensation of hexabromobenzene with 3-hydroxy-3,3-diphenylpropyne. This new sexipedal host forms inclusion compounds with dioxane, γ-butyrolactone, dimethylformamide (DMF) and dimethylsulfoxide, all with H:G = 1:6, acetone (1:3), tetrahydrofuran (1:4) and cyclohexanone (1:5). The crystal structure[†] of the dimethylformamide inclusion compound is shown in Fig. 1.

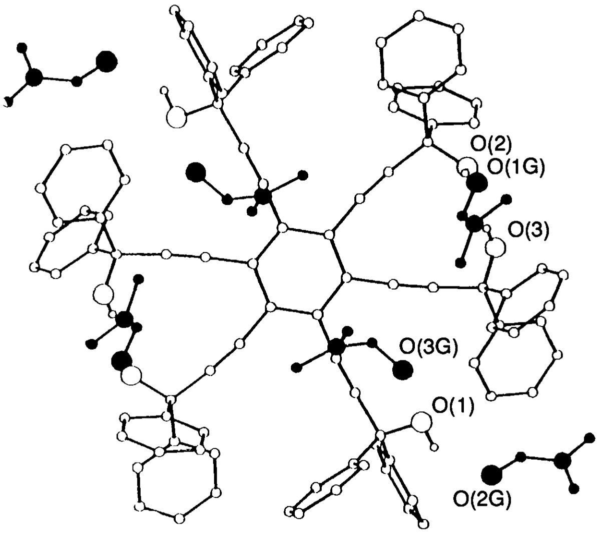

Fig. 1 Molecular structure of the inclusion compound, with DMF molecules shaded

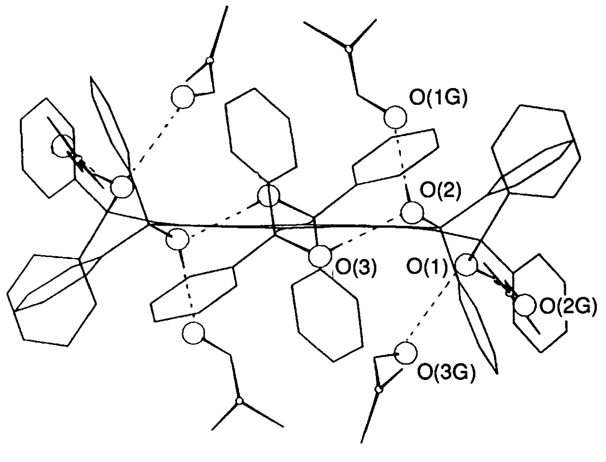

Fig. 2 The host's hydroxy moieties are located alternately above and below the central plane. Hydrogen bonds are indicated by dashed lines.

The host molecule is situated on a centre of inversion and the hydroxy moeties are located alternately above and below the plane defined by the benzene ring, as shown in Fig. 2. The DMF guests are not symmetrically arranged about the host molecule. There is an intramolecular hydrogen bond [O(3)···O(2) = 2.853(4) Å] and one DMF molecule is in turn hydrogen bonded to O(2) [O(2)···O(1G) = 2.594(6) Å]. A second DMF is strongly hydrogen bonded to the host, *via* O(1)···O(2G) [2.661(6) Å], but the third DMF is weakly held [O(1)···O(3G) = 2.929(8) Å]. The thermal analysis is shown in Fig. 3. TG confirmed the host: guest stoichiometry obtained in the crystal structure. A total weight loss of 24.9% was observed,

---

[†] *Crystal data for* $\mathbf{1}\cdot(DMF)_6$. *M* 1754.06, triclinic, space group $P\bar{1}$, a = 9.412(4), b = 16.176(8), c = 16.585(5) Å, α = 81.64(3)°, β = 85.76(3)°, γ = 80.68(4)°, V = 2462(2) Å^3, Z = 1, D_c = 1.183 g cm^{-3}, μ (Mo-Kα) = 0.077 mm^{-1}, $F(000)$ = 930, crystal size = 0.22 × 0.38 × 0.38 mm. Data were collected at 293 K using an Enraf–Nonius CAD4 diffractometer and Mo-Kα radiation (λ = 0.7107 Å) with θ_{max} = 25° ($\omega - 2\theta$ scans). The structure was solved using direct methods[8] and refined[9] on all 8638 F^2 values with anisotropic displacement parameters for all non-hydrogen atoms of the host as well as oxygen and nitrogen atoms on the guests. Hydroxy hydrogen atoms were located in the difference Fourier map and included in the final model at a constrained distance [1.00(3) Å] from their parent atoms. Final $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]^2\}^{\frac{1}{2}}$ = 0.286 for all data, conventional R on F values for 5083 data with $F_o^2 > 2\sigma(F_o)^2$ = 0.095, goodness of fit = 1.04 on F^2 values.

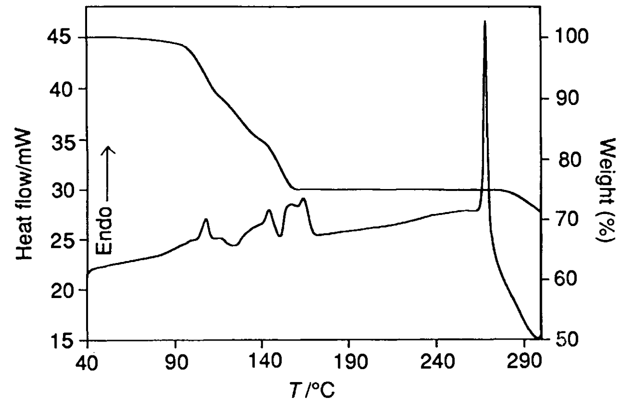

Fig. 3 DSC and TG traces for **1**·(DMF)$_6$

which correlates well with the expected loss of 25.0% for a 1 : 6 ratio. As *Fig. 3* shows, the guest loss occurs in three equal steps, each caused by the desorption of two DMF molecules. These steps correspond to the first three endotherms seen in the DSC between 80 and 170 °C. The DSC also shows a sharp melting point for the host compound at onset temperature 267 °C.

References

1 E. Weber, *Inclusion Compounds, Vol 4,* ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, 1991.
2 E. Weber and H.-P. Josel, *J. Incl. Phenom.*, 1983, **1**, 79.
3 F. Toda and K. Akagi, *Tetrahedron Lett.*, 1968, **33**, 3695.
4 D. R. Bond, L. Johnson, L. R. Nassimbeni and F. Toda, *J. Solid State Chem.*, 1991, **92**, 68.
5 E. Weber, K. Skobridis, A. Wierig, L. R. Nassimbeni and L. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2123.
6 L. Johnson, L. R. Nassimbeni, E. Weber and K. Skobridis, *J. Chem. Soc., Perkin Trans 2.* 1992, 2131.
7 D. D. MacNicol, *Inclusion Compounds, Vol. 2,* Academic Press, London, 1985, ch. 5, p. 123.
8 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
9 G. M. Sheldrick, SHELXL93, *J. Appl. Crystallogr.*, in preparation.

Paper 4/04170D
Received 8*th July* 1994
Accepted 26*th July* 1994