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Clathrate tetraldehyde cavitand: single-crystal structure and NMR study

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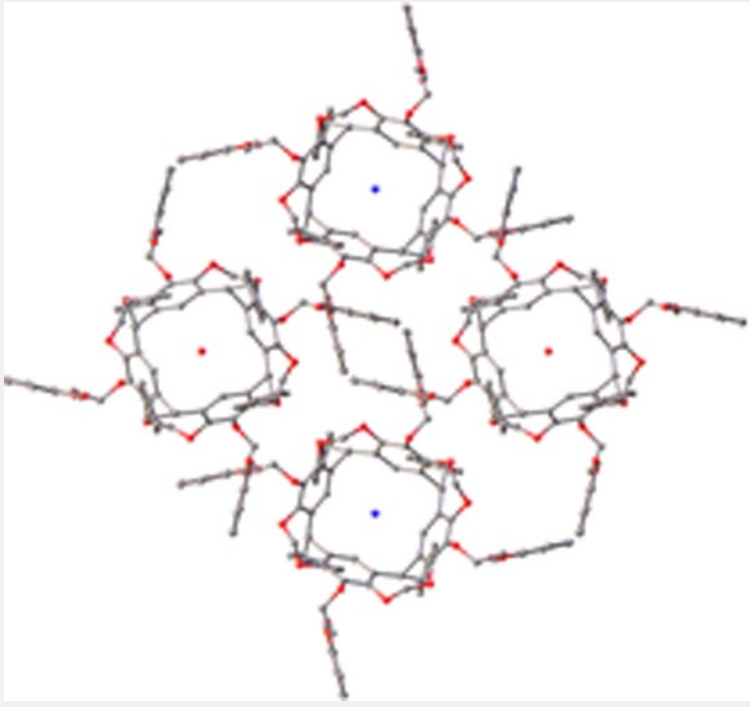
ABSTRACT

The tetraldehyde cavitand, $C_{100}H_{88}O_{20}$, was synthesised as the penultimate stage of a procedure to obtain cavitand-capped porphyrins. The complete structural characterisation was performed by single-crystal X-ray diffraction studies, NMR and IR spectroscopy. The inclusion phenomena of the solvent molecules were confirmed using NMR spectroscopy. The structure is the first example of a clathrate having an aromatic tetraldehyde cavitand grown as a single crystal with acetonitrile at the lower rim of the molecule and methanol at the upper rim of the molecule.



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KEYWORDS
Tetraldehyde cavitand; molecular recognition; crystal structure; NMR; TGA

1. Introduction

The 'molecular recognition' concept (*1*) has led to an ever growing field of molecular containers having expanded inner cavities capable of accommodating sizable or multiple guests. This concept has been applied to fields such as separation science, drug delivery systems and molecular sensing and recognition (*2*). In particular, the host–guest complex can enhance the chemical stability of the guest and the subsequent release of products (*3*). The non-covalent but intimate contact of the host–guest system can render changes in physical and/or chemical properties of the guest as well as the host. Hemicarcerand and carceplex materials have inspired a number of researchers to prepare a wide range of building blocks having host–guest binding properties (*4*). As a result, novel chemistry methods have been developed in order to improve the size selectivity of molecular containers. However, typically these procedures involve multiple organic synthetic

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steps, purification steps which yield target hosts in very low yield. In an attempt to improve this situation and broaden the field, new synthesises and approaches have been attempted including metal–ligand self-assembly and hydrogen-bonding self-assembly (*5*). Efforts have also been made to modify the head groups of the upper rim of the cavitands to enhance the total volume of the cavity using Suzuki cross-coupling, Heck coupling or by bridging the resorcinarene hydroxyl groups with different functionalised derivatives (*6*). In particular, Williamson ether synthesis has been applied (*4*, *7*).

Herein, we report on the crystal structure of a clathrate tetraldehyde cavitand, and further characterisation of this deepened tetraldehyde cavitand, which was synthesised as the penultimate stage in the synthesis of a cavitand-capped porphyrin.

2. Result and discussion

The structure is the first example of a clathrate tetraldehyde cavitand having an aromatic aldehyde at the upper rim of the molecule. Disordered methanol, as well as acetonitrile, co-crystallised as guests (Scheme 1).

In this study, we compare (Scheme 2) our novel structure (**1**) to a compound reported by us previously having the same 'head groups' with a different spacer group and 'feet' (*8*). Both of these tetraldehyde cavitands have been synthesised at the penultimate stage of the synthesis of cavitand-capped porphyrins. The clathrate tetraldehyde cavitand **1** is completely soluble in ethyl acetate, methylene chloride, chloroform, acetonitrile, and THF and is insoluble in methanol and ethanol. The X-ray data are summarised in Table 1 (Supplementary material). Compound **1** has all four aromatic aldehyde groups in a similar arrangement at the upper rim, **2** exhibits two different orientations of these groups: in one orientation, two adjacent aldehyde groups appear upright and the remaining two appear splayed, perpendicular to the first two (Figure 1).

Compound **1** is a methanol-acetonitrile clathrate, while each of the cavitands for **2** contained one ethyl acetate molecule which was highly disordered and was removed using *SQUEEZE* (*9*) in final refinement. The present tetraldehyde **1** has methanol at the centre of the upper rim bound with four C–O–π interactions (Table 2, Supplementary material). In the lower rim, the acetonitrile molecule is bound with four C–H–N short contacts (where C–H–N: 3.717 Å, C–H: 0.987 Å, H–N: 2.73 Å, C–H–N: 175.29°). The methanol oxygen and acetonitrile nitrogen atoms are exactly opposite to each other. The distance between the methanol carbon and the acetonitrile carbon is 4.16 Å. The asymmetric units of the tetraldehyde through the 001 *axes* show the arrangement of the head group and the methanol guest in the upper rim, whilst acetonitrile is the guest in the lower rim.

In the packing arrangement (Figure S1, Supplementary material), the cavitand **1** demonstrates intermolecular contacts via C–H–O interactions (Table 2, Supplementary material) in a head-to-head arrangement. The head-to-tail interactions occur via the aromatic C–H of the feet to the head oxygen and C–H–π interactions (Table 2, Supplementary material), whilst the head-to-head interactions occur via the aldehyde oxygen to aldehyde C–H and ether oxygen to aldehyde C–H. The ether oxygen to aldehyde oxygen close contacts keep the upper rim bent and downwards. In this scenario, one can see that in the

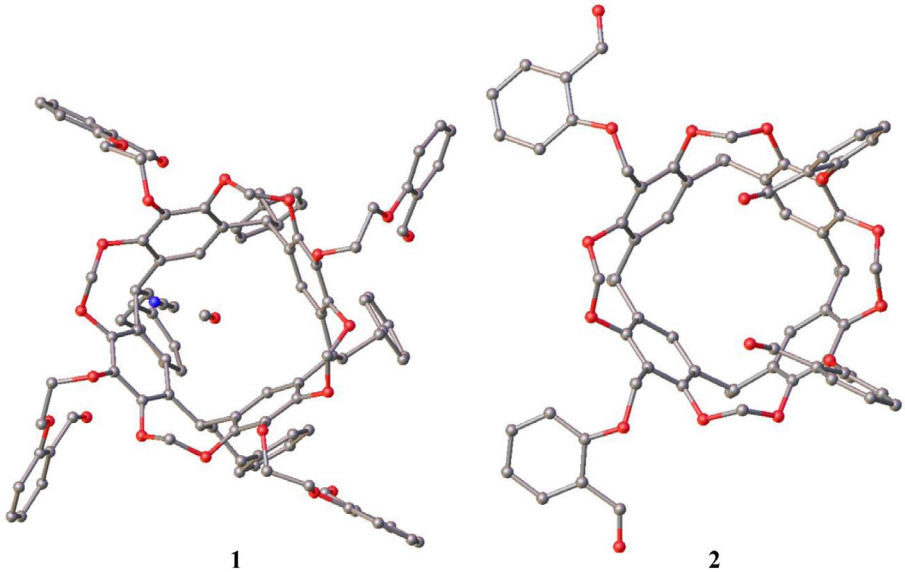


Figure 1. (Colour online) Asymetric unit of tetraldehyde cavitand **1** and **2**.

head-to-feet and feet-to-head arrangements, guest solvents have opposite functional groups to each other. The C–H–π interactions (Table 2, Supplementary material) also play significant roles to shape the flower structure of the tetraldehyde cavitand. The reported tetraldehyde **2** fashioned head-to-tail arrangements via C–H–O and C–H–π interactions, the splayed aldehyde arms make layers and are organised in a stair-like structure, whilst the aldehyde groups perpendicular to the splayed arms make a zigzag-layered structure. The π–π interactions (Table 3, Supplementary material) in the tetraldehyde cavitand **1** extend vertically through the *a*-axis and make a layer-like structure.

The recognition of solvent was confirmed by ^{1}H NMR studies carried out in deuterated chloroform. In this solvent, nearly all the signals of the cavitand underwent upfield shifts and peak splitting in the presence of methanol and methanol with acetonitrile (Figure 2). Moreover, the most remarkable shifts were observed in the presence of methanol for protons ArH 7.80–7.75 and 7.52–7.47 ppm. The singlet of the aldehyde group shifted from 10.31 to 10.26 ppm and the peak split in the presence of methanol. In addition, the protons of the ethyl bridge, as well as the protons located in the lower rim ethyl moiety shifted from 4.33 to 4.29, 4.72 to 4.69, 5.64 to 5.62, 2.42 to 2.41 and 2.61 to 2.58 ppm, respectively. These upfield shifts are in agreement with the transformation of hydrogen-bonding established in the cavitand.

A more significant change was observed for protons located in the lower rim ethyl moiety when acetonitrile alone was recognised, where linkers may be between the nitrile group and the lower rim ethyl groups, which occurred at 2.39–2.46 and 2.59–2.63 ppm in the free cavitand and at 2.45–2.47 and 2.58–2.61 ppm in the acetonitrile clathrate. This unusual peak shift is rationalised by the unique position of the protons. Noticeable is that there is no peak splitting observed for only acetonitrile recognition.

Thermogravimetric analysis (Figure 3) for **1** shows that weight loss in the range of 26–176 °C is 4.32%, corresponding to the loss of one acetonitrile (2.43%) and one methanol (1.90%) molecules (calc. 4.34%), indicating that none of the crystallised solvent loss occurred at room temperature. On raising the temperature, slowly decomposition started and continuous weight loss was observed up to 600 °C. The decomposition took place in two steps. In the range of 176–425 °C, a 47.5% mass loss occurred, which is also further divided into two steps and one can observe this in the DTG trace. This may be oxidative degradation or formation of different reactive species during this step. The second decomposition of 47.6% takes place in the temperature range of 425–555 °C and is probably due to the destruction of the complete molecule, leaving behind a negligible amount of unreactive ash mass.

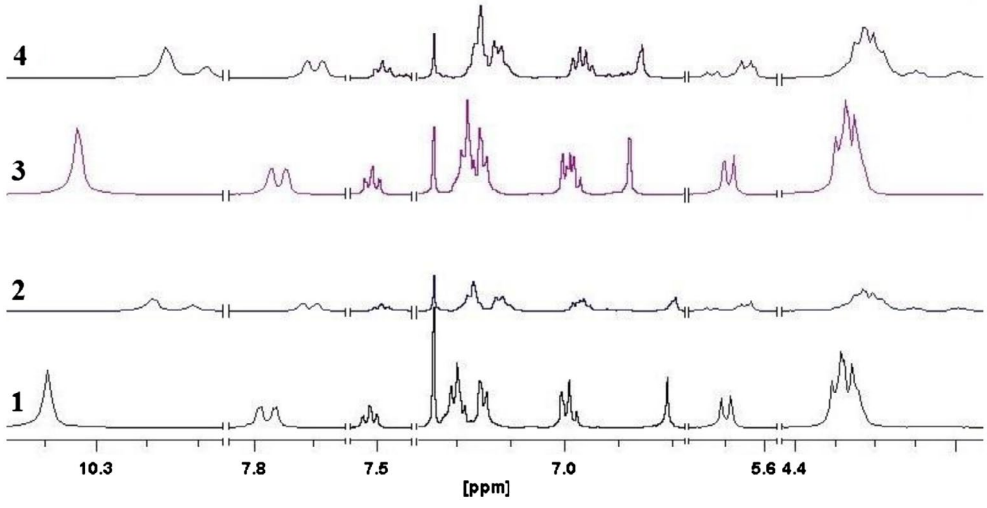


Figure 2. (Colour online) NMR of **1** in $CDCl_3$ (1), **1** with methanol (2), **1** with acetonitrile (3) and **1** with methanol and acetonitrile (4).

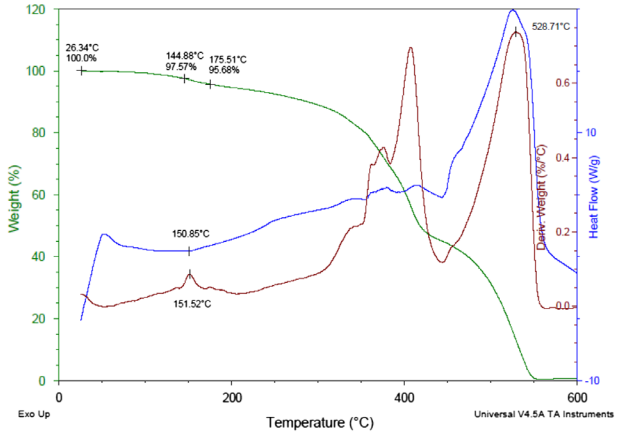


Figure 3. (Colour online) DSC and TG-DTG of **1**.

3. Conclusion

The clathrate tetraldehyde cavitand **1** has a deep enough cavity to act as host, is completely soluble in ethyl acetate, methylene chloride, chloroform, acetonitrile and THF and is insoluble in methanol and ethanol. The structure of the cavitand was confirmed by single-crystal X-ray analysis. The crystal analysis gave insight into the host–guest nature of these molecules and the stabilisation of solid state structures via C–H…O, C–H…π, C–O…π and π–π interactions in the packing arrangement. The NMR solution phase results were complimented by the single-crystal structure analysis. The TG-DTG results support that no guest release occurred at room temperature.

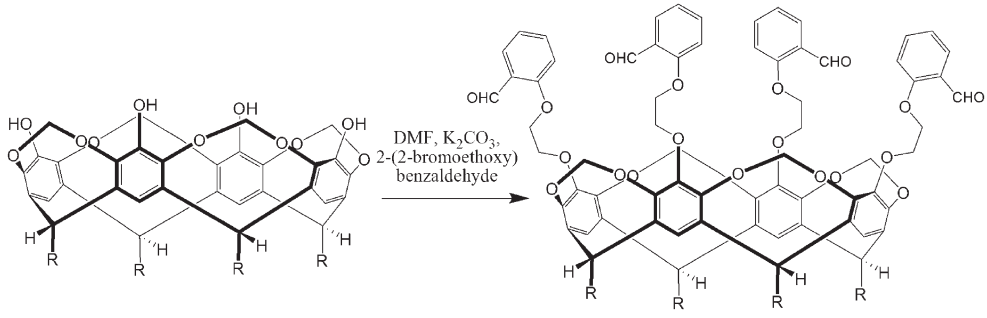
4. Experimental

4.1. Synthesis of tetraldehyde cavitand

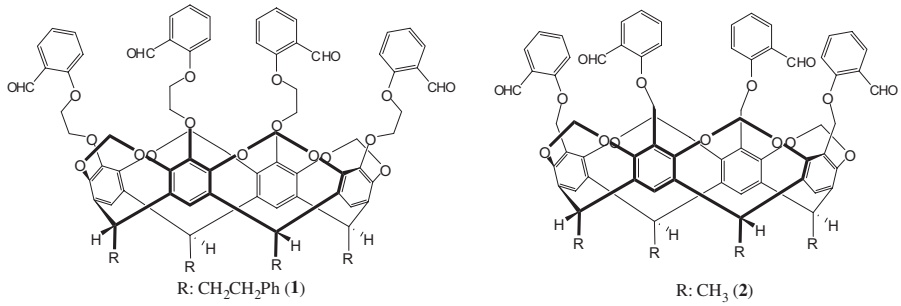
To the stirring solution of oven-dried (100 °C) K_2CO_3 (0.69 g, 5.00 mmol) in dry dimethylformamide (40 ml), the tetrolcavitand (0.50 g, 0.490 mmol) (*4*, *10*) was added and stirred until completely dissolved. To the resulting solution, 2-(2-bromoethoxy)benzaldehyde (0.90 g, 3.93 mmol) was added and the reaction mixture gently heated at 55 °C for three days. During this period, the solution became cloudy and a precipitate started to form on the sides of the reaction flask. The reaction mixture was cooled to room temperature and filtered. The filtrate was collected and evaporated under vacuum. The oily residue was stirred with methanol overnight, filtered and washed with methanol to obtain a pure white compound. (0.74 g, 93% yield), Mp 106–108 °C. (Figures S2–S4 in Supplementary material) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.39–2.46 (m, 8H, CH_2CH_2Ph), 2.59–2.63 (m, 8H, CH_2CH_2Ph), 4.33 (m, 20H, inner of OCH_2O and OCH_2CH_2O), 4.72 (t, 4H, CH), 5.64 (d, 4H, outer of OCH_2O), 6.80 (S, 4H, Cavitand Ar–H), 6.99 (m, 4H, Ar–H), 7.16 (m, 4H, Ar–H), 7.18–7.24 (m, 20H, CH_2CH_2Ph), 7.52 (td, 4H, Ar–H), 7.80 (dd, 4H, Ar–H), 10.31 (s, 4H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 189.9, 161.3, 148.4, 144.3, 141.9, 138.9, 136.0, 128.2, 128.0, 126.1, 125.1, 121.0, 114.4, 112.9, 99.4, 71.5, 68.3, 37.1, 34.5, 32.3. FT-IR/ATR, cm^{-1}: 2939, 2870, 1683, 1599, 1480, 1455, 1438, 1315, 1286, 1188, 1155, 1103, 1018, 980, 938, 831, 752, 697, 654, 587. Anal. Calcd. for $C_{100}H_{88}O_{20}$: C, 74.61; H, 5.51. Found: C, 74.73; H, 5.57%.

4.2. Materials and methods

All chemicals were purchased from Aldrich. The chemical reagents were laboratory grade and unless stated otherwise used without further purification. The tetraldehyde cavitand was synthesised from the tetrolcavitand as per the reported method (*10*). The IR spectra were recorded using a PerkinElmer Universal ATR spectrometer. NMR spectra were recorded employing Bruker Avance 400 & 600 MHz instruments with $CDCl_3$ as the solvent. The DSC and TG-DTG experiments were conducted using a SDT Q600 V20.9 (TA Instruments, USA) equipped with Universal



Scheme 1. Synthesis of tetraldehyde cavitand.



Scheme 2. Tetraldehdye cavitands.

Analysis 2000 software (version 4.5A). The tetraldehyde cavitand was accurately weighed into crimped aluminium pans and subjected to a thermal scan from room temperature to 600 °C at a heating rate of 10.0 °C/min.

4.3. Data collection and refinement

Single-crystal X-ray diffraction data were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection was carried out at 173(2) K. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT (*11*). The data were scaled and absorption correction performed using SADABS (*11*). The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods based on F^2 using SHELXL-97 (*12*). The program Olex2 was used to prepare molecular graphic images (*13*). All hydrogen atoms, except those of the solvent molecules (acetonitrile and methanol), were placed in idealised positions and refined in riding models with U_{iso} assigned the values to be 1.2 or 1.5 times those of their parent atoms and the constraint distances of C–H ranging from 0.95 to 1.00 Å. The hydrogen atoms of the solvent molecules are excluded from the structure model, due to the fact that the solvent molecules are situated on special positions with four fold symmetry. The anisotropic displacement parameters (ADP) of most atoms were restrained. The atoms C7A, C7B, C8, O4, O5, C9 to C15 were all refined with site occupancy factors of 0.50. C7A and C7B were constrained at the same position with the same ADP. There is a solvent accessible void of 148 Å^3 per unit cell, which could not be modelled as discrete atomic sites, probably due to disorder. The program PLATON SQUEEZE was employed to calculate the contribution to the diffraction from the missing solvent molecules and it produced a set of partial-solvent-free diffraction intensities (*9*). This set of intensities was used for final refinements. SQUEEZE estimated a total count of 86 electrons per unit cell contributed by the missing solvents, which were excluded in the formula and subsequent calculation of molecular weight, density etc. (*9*).

Supplemental material

^{1}H NMR, ^{13}C NMR and COSY spectra are given in the supporting material available here: http://dx.doi.org/10.1080/10610278.2015.1102261. CCDC-989879 and 726325 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223/336 033; email: deposit@ccdc.ac.uk

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Disclosure statement

No potential conflict of interest was reported by the authors.

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