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# Structure of the $\gamma$-Cyclodextrin–1-Propanol–17$H_2O$ Inclusion Complex*

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## Abstract

The crystal structure of the hydrated 1-propanol inclusion complex of $\gamma$-cyclodextrin ($\gamma$-CD), $C_{48}H_{80}O_{40}.C_3H_8O.17{\cdot}0H_2O$, was determined from two sets of X-ray diffraction data collected from two crystals grown in different batches; the results are practically identical except for a few occupancy factors of water molecules and hydrogen-bonding interactions involving O(6) and water molecules. Both crystals have tetragonal space group $P42_12$ with cell dimensions: $a = b = 23{\cdot}840$ (5), $c = 23{\cdot}227$ (5) Å, and $a = b = 23{\cdot}8093$ (5), $c = 23{\cdot}2069$ (6) Å, respectively, $Z = 6$. The structures were refined by the blocked full-matrix least-squares method to $R$ factors of 0·067 for 5029 unique observed reflections $[I \geq 3\sigma(I)]$ and 0·082 for 4303 unique observed reflections, respectively. The $\gamma$-CD molecules are stacked on top of each other, their axes coinciding with the crystal fourfold rotation axis. Within the same stack, three independent $\gamma$-CD molecules are in tail-to-tail, head-to-head and head-to-tail arrangements, and hydrogen bonds are formed between the adjacent $\gamma$-CD molecules with the O(2), O(3) and O(6) hydroxyls. The cavities of the $\gamma$-CD molecules form endless 'major' channels. They accommodate 3·1 water molecules distributed over eight sites and the 1-propanol molecules which, however, could not be traced unambiguously owing to crystallographic disorder around the fourfold axis. The 'minor' interstitial channels between the stacks of $\gamma$-CD molecules are filled with 9·7 water molecules distributed over 12 sites which are involved in a complicated hydrogen-bonding network to primary and secondary hydroxyls of $\gamma$-CD molecules. There are 12·8 $H_2O$ in the asymmetric unit, or $12{\cdot}8 \times 8/6 = 17{\cdot}0$ $H_2O$ per $\gamma$-CD molecule, as given in the title. All glucose residues are in the usual $^4C_1$ chair conformation with minor distortion. In the series $\alpha$-, $\beta$-, $\gamma$-CD, the C(4)—O(4)—C(1)′ interglucose bond angles reduce from 119·0 to 117·7 to 116·8°. The average O(2)···O(3)′ intramolecular hydrogen-bonding distances between adjacent glucoses for $\gamma$-CD is 2·83 Å, much shorter than for $\alpha$-CD (about 3·00 Å), but nearly the same as for $\beta$-CD, indicating a tighter ring of hydrogen bonds around the O(2), O(3) rims in $\beta$- and $\gamma$-CD than in $\alpha$-CD. The O(6) hydroxyl groups of glucoses 1 to 5 are twofold disordered with the major occupation sites pointing 'away' from the molecular cavity, while the minor occupation sites point 'inward'.

## Introduction

The cyclodextrins (CD's), also called cycloamyloses, are a family of macrocyclic oligosaccharides consisting of six ($\alpha$-CD), seven ($\beta$-CD), or eight ($\gamma$-CD) D-glucose units in the $^4C_1$ chair conformation and linked by $\alpha$-1,4-interglycosidic bonds (Saenger, 1980, 1984; Szejtli, 1982). They have a 'round', slightly conical form with all the secondary hydroxyl groups O(2)—H and O(3)—H located on the wider end and all the primary hydroxyl groups O(6)—H on the narrower end, and an intramolecular relatively hydrophobic cavity whose surface is dominated by H atoms and glycosidic O atoms. Because of the intramolecular cavity, cyclodextrins have the ability to form inclusion complexes with a wide variety of molecules and ions that are of suitable size to fit into it (Szejtli, 1982; Saenger, 1984). This is the reason why cyclodextrins have been used successfully as models to study non-covalent intermolecular interactions and enzyme mechanisms. Since the guest molecule is encapsulated by CD in the inclusion complex, it may show changes in its chemical and physical properties, which is of advantage in industrial applications (Szejtli, 1982).

X-ray studies of a large number of crystalline complexes of $\alpha$-CD and $\beta$-CD have revealed geometrical features of the host–guest interaction as well as the conformation of the macrocyclic ring, and chemical and physical properties of the inclusion complexes have been interpreted on that basis. In the crystal structures, the C(6)—O(6) bonds are usually directed 'away' from the centre of the cyclodextrin ring to form hydrogen bonds with solvent molecules and neighboring CD molecules. They can, however, turn 'inward' owing to hydrogen bonding between the O(6)—H group and guest molecules included within the cavity. Intramolecular hydrogen bonds

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O(2)—H···O(3) or O(3)—H···O(2) exist between the secondary hydroxyl groups of adjacent glucose units for almost all CD molecules. Only a few crystal structures have been reported for γ-CD hydrate (MacLennan & Stezowski, 1980; Harata, 1987) and its inclusion complexes (Kamitori, Hirotsu & Higuchi, 1986, 1988). In the preliminary paper of this study (Lindner & Saenger, 1980) we reported on the channel-type structure of the hydrated γ-CD–1-propanol inclusion complex. Because of the low accuracy of this previous structure analysis ($R = 0{\cdot}14$ with space group $P4$), we did not discuss in detail the bonding geometry, the conformation of the macrocycle and the arrangement of the solvent molecules. We have re-determined the structure on the basis of the actual space group $P42_12$ and have achieved much better results, with high accuracy, which are reported in this paper. Since β-CD crystal structures show differences in the hydration pattern depending on crystallization batches (Fujiwara *et al.*, 1983; Steiner, 1990), two different crystals of the γ-CD–1-propanol hydrate were investigated in this study.

Table 1. *Crystallographic data*

| | Crystal (1) | Crystal (2) |
|---|---|---|
| $a$ (Å) | 23·840 (5) | 23·8093 (5) |
| $b$ (Å) | 23·840 (5) | 23·8093 (5) |
| $c$ (Å) | 23·227 (6) | 23·2069 (5) |
| $V$ (Å$^3$) | 13201 (5) | 13155·6 (5) |
| Space group | $P42_12$ | $P42_12$ |
| $Z$ | 6 | 6 |
| Formula | $C_{48}H_{80}O_{40}.C_3H_8O.xH_2O$<br>$x = 17{\cdot}00$ | $C_{48}H_{80}H_{40}.C_3H_8O.xH_2O$<br>$x = 17{\cdot}12$ |
| Data collection | | |
| Crystal size (mm) | 0·40 × 0·20 × 0·20 | 0·40 × 0·20 × 0·20 |
| Diffractometer | Stoe four-circle | Enraf–Nonius CAD-4 |
| Radiation (Å) | Cu $K\alpha$, 1·54 | Cu $K\alpha$, 1·54 |
| Monochromator | Ni filter | Ni filter |
| Temperature (K) | 298 | 298 |
| Scan mode | $\omega/2\theta$ | $\omega/2\theta$ |
| $\theta$ range (°)* | $2 \leq \theta \leq 60$ | $2 \leq \theta \leq 49$ |
| $hkl$ range† | $h$ 0→23 | 0→23 |
| | $k$ 0→23 | 0→23 |
| | $l$ 0→23 | 0→22 |
| No. of reflections | 7470 | 5866 |
| No. of unique reflections | 6783 | 5459 |
| No. of reflections with $I \geq 3\sigma(I)$ | 5029 | 4303 |
| $R_{\text{merge}}$ | 0·023 | 0·028 |
| $R$ factor | 0·067 | 0·082 |

* The scan range for crystal (2) was physically limited by the diffractometer hardware.

† Not all of the reflections were collected for crystal (2) due to the limited scan range.

## Experimental

### *Crystallization*

Crystals suitable for X-ray diffraction were obtained by slow cooling of hot (~ 343 K) saturated solutions of γ-CD in 60% (*v*/*v*) 1-propanol. The crystals were colorless transparent square bipyramids truncated at both ends.

### *Data collection*

In order to determine the correct space group, $P4$ or $P42_12$, X-ray diffraction data were collected on two crystals grown in different batches at different times. Crystals with dimensions 0·40 × 0·20 × 0·20 mm were sealed in glass capillaries with a drop of mother liquor to avoid any crystal dehydration and used for X-ray diffraction measurements, see Table 1. Accurate cell dimensions were obtained by refining against the well-determined angular settings of 18 reflections in the 2θ range 10–50°. The first set of data [crystal (1)] was collected on a Stoe four-circle automated diffractometer using X-rays from a sealed tube, and the second set of data [crystal (2)] on an Enraf–Nonius CAD-4 automated diffractometer using X-rays from a rotating-anode generator. The data were corrected for Lorentz and polarization effects together with an empirical absorption correction (Walker & Stuart, 1983).

### *Structure refinement*

The structure solution was based on the assumption that the γ-CD–1-propanol inclusion complex is isomorphous with γ-CD–12-crown-4–NaCl (Kamitori, Hirotsu & Higuchi, 1988) with space group $P42_12$. The atomic positions of C and O atoms [except O(6)] of the γ-CD molecule from the crown-ether complex were utilized for the γ-CD–1-propanol data. The Fourier synthesis based on phases calculated from these atomic coordinates revealed the positions of some of the O(6) atoms and some of the water O atoms. Refinement continued with assignment of the remaining disordered O(6) and water O atoms. All of the non-H atoms were refined anisotropically. The positions of H atoms attached to the C atoms were calculated theoretically and their collective isotropic temperature factor was refined. The reflections with $I \geq 3\sigma(I)$ [5029 and 4303 reflections for the two crystals (1) and (2)] were regarded as observed and used in the final refinements. In the last cycle of refinement the average parameter shifts were less then 1/4 of the average errors determined from the correlation matrix. The final difference density calculations showed $\Delta\rho$ within $+0{\cdot}29$ and $-0{\cdot}28$ e Å$^{-3}$ (1) and $+0{\cdot}49$ and $-0{\cdot}43$ e Å$^{-3}$ (2), and the final $R$ factors ($R = \sum||F_o| - |F_c||/\sum|F_o|$) were 0·067 and 0·082 for the two data sets. 20 sites accounting in total for occupancies of 12·8 water molecules were located for each crystal structure. The included 1-propanol molecules could not be traced unambiguously owing to their disordered position close to or on the fourfold axis.

Table 2. *Fractional coordinates and equivalent isotropic temperature factors* (Å$^2$) *for crystal* (1)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3$ where $U_{ii}$ are the diagonal elements of the diagonalized orthogonalized $U_{ij}$ tensor. Standard deviations are given in parentheses.

| | $x$ | $y$ | $z$ | $U_{eq}$ | Occupancy |
|---|---|---|---|---|---|
| Molecule *A* | | | | | |
| C(1)1 | 0·6683 (3) | 0·2369 (3) | 0·9504 (3) | 0·091 (8) | 1·00 |
| C(2)1 | 0·7051 (3) | 0·2270 (3) | 0·8989 (3) | 0·093 (8) | 1·00 |
| C(3)1 | 0·7111 (3) | 0·1609 (3) | 0·8911 (3) | 0·091 (8) | 1·00 |
| C(4)1 | 0·7327 (3) | 0·1345 (3) | 0·9470 (3) | 0·094 (8) | 1·00 |
| C(5)1 | 0·6919 (3) | 0·1497 (3) | 0·9963 (4) | 0·101 (9) | 1·00 |
| C(6)1 | 0·7134 (5) | 0·1257 (4) | 1·0542 (4) | 0·119 (9) | 1·00 |
| O(2)1 | 0·6810 (2) | 0·2505 (2) | 0·8494 (2) | 0·099 (6) | 1·00 |
| O(3)1 | 0·7511 (2) | 0·1507 (2) | 0·8442 (2) | 0·104 (6) | 1·00 |
| O(4)1 | 0·7346 (2) | 0·0762 (2) | 0·9381 (2) | 0·095 (6) | 1·00 |
| O(5)1 | 0·6882 (2) | 0·2096 (2) | 1·0000 (2) | 0·097 (6) | 1·00 |
| O(6)1*A* | 0·7722 (4) | 0·1422 (4) | 1·0634 (4) | 0·117 (9) | 0·65 |
| O(6)1*B* | 0·6659 (9) | 0·1384 (7) | 1·0959 (6) | 0·16 (1) | 0·35 |
| C(1)2 | 0·4501 (3) | 0·2874 (4) | 0·9498 (4) | 0·099 (9) | 1·00 |
| C(2)2 | 0·4874 (3) | 0·3040 (3) | 0·8988 (3) | 0·095 (8) | 1·00 |
| C(3)2 | 0·5359 (3) | 0·2640 (4) | 0·8913 (3) | 0·098 (8) | 1·00 |
| C(4)2 | 0·5684 (3) | 0·2603 (3) | 0·9456 (3) | 0·090 (8) | 1·00 |
| C(5)2 | 0·5310 (3) | 0·2425 (4) | 0·9958 (3) | 0·103 (9) | 1.00 |
| C(6)2 | 0·5615 (4) | 0·2375 (4) | 1·0521 (4) | 0·119 (9) | 1·00 |
| O(2)2 | 0·4522 (2) | 0·3051 (2) | 0·8470 (2) | 0·114 (7) | 1·00 |
| O(3)2 | 0·5708 (2) | 0·2842 (2) | 0·8443 (2) | 0·114 (7) | 1.00 |
| O(4)2 | 0·6125 (2) | 0·2200 (2) | 0·9376 (2) | 0·093 (6) | 1·00 |
| O(5)2 | 0·4855 (2) | 0·2815 (2) | 0·9995 (2) | 0·109 (6) | 1·00 |
| O(6)2*A* | 0·5912 (3) | 0·2893 (4) | 1·0622 (3) | 0·142 (9) | 0·75 |
| O(6)2*B* | 0·526 (1) | 0·218 (1) | 1·0950 (8) | 0·17 (1) | 0·25 |
| Molecule *B* | | | | | |
| C(1)3 | 0·6375 (3) | 0·2547 (3) | 0·6278 (4) | 0·097 (8) | 1·00 |
| C(2)3 | 0·6109 (3) | 0·2835 (3) | 0·6794 (4) | 0·100 (9) | 1·00 |
| C(3)3 | 0·5532 (3) | 0·2621 (4) | 0·6881 (3) | 0·097 (8) | 1·00 |
| C(4)3 | 0·5186 (3) | 0·2686 (3) | 0·6322 (3) | 0·093 (8) | 1·00 |
| C(5)3 | 0·5490 (3) | 0·2359 (3) | 0·5856 (3) | 0·099 (8) | 1.00 |
| C(6)3 | 0·5191 (4) | 0·2418 (5) | 0·5265 (4) | 0·13 (1) | 1·00 |
| O(2)3 | 0·6449 (2) | 0·2784 (2) | 0·7305 (2) | 0·106 (6) | 1·00 |
| O(3)3 | 0·5239 (2) | 0·2941 (2) | 0·7323 (2) | 0·108 (6) | 1·00 |
| O(4)3 | 0·4648 (2) | 0·2451 (2) | 0·6422 (2) | 0·095 (6) | 1·00 |
| O(5)3 | 0·6051 (2) | 0·2588 (2) | 0·5785 (2) | 0·103 (6) | 1·00 |
| O(6)3*A* | 0·5176 (3) | 0·2962 (4) | 0·5055 (3) | 0·144 (9) | 0·83 |
| O(6)3*B* | 0·555 (1) | 0·224 (2) | 0·4854 (9) | 0·13 (1) | 0·17 |
| C(1)4 | 0·7784 (4) | 0·0817 (3) | 0·6275 (4) | 0·108 (9) | 1·00 |
| C(2)4 | 0·7776 (3) | 0·1220 (3) | 0·6785 (4) | 0·094 (8) | 1·00 |
| C(3)4 | 0·7217 (3) | 0·1464 (3) | 0·6886 (3) | 0·094 (8) | 1·00 |
| C(4)4 | 0·7012 (3) | 0·1749 (3) | 0·6332 (3) | 0·091 (8) | 1·00 |
| C(5)4 | 0·7036 (4) | 0·1335 (4) | 0·5840 (3) | 0·104 (9) | 1·00 |
| C(6)4 | 0·6811 (5) | 0·1535 (5) | 0·5273 (4) | 0·16 (1) | 1·00 |
| O(2)4 | 0·8007 (2) | 0·0961 (2) | 0·7286 (2) | 0·109 (6) | 1·00 |
| O(3)4 | 0·7210 (2) | 0·1873 (2) | 0·7343 (2) | 0·094 (6) | 1·00 |
| O(4)4 | 0·6466 (2) | 0·1974 (2) | 0·6425 (2) | 0·094 (6) | 1·00 |
| O(5)4 | 0·7563 (3) | 0·1093 (2) | 0·5777 (2) | 0·109 (6) | 1·00 |
| O(6)4*A* | 0·7183 (4) | 0·1936 (4) | 0·5097 (3) | 0·131 (9) | 0·69 |
| O(6)4*B* | 0·715 (1) | 0·141 (10) | 0·4803 (7) | 0·18 (1) | 0·31 |
| Molecule *C* | | | | | |
| C(1)5 | 0·7400 (3) | 0·1591 (3) | 0·2816 (4) | 0·097 (8) | 1·00 |
| C(2)5 | 0·7737 (3) | 0·1351 (3) | 0·2305 (4) | 0·100 (9) | 1·00 |
| C(3)5 | 0·7595 (3) | 0·0742 (3) | 0·2214 (3) | 0·099 (8) | 1·00 |
| C(4)5 | 0·7639 (4) | 0·0413 (3) | 0·2770 (4) | 0·110 (9) | 1·00 |
| C(5)5 | 0·7289 (4) | 0·0684 (3) | 0·3241 (4) | 0·105 (9) | 1·00 |
| C(6)5 | 0·7324 (5) | 0·0394 (4) | 0·3826 (4) | 0·14 (1) | 1·00 |
| O(2)5 | 0·7659 (2) | 0·1685 (2) | 0·1793 (2) | 0·113 (6) | 1·00 |
| O(3)5 | 0·7966 (3) | 0·0506 (2) | 0·1776 (3) | 0·126 (7) | 1·00 |
| O(4)5 | 0·7479 (2) | −0·0147 (2) | 0·2659 (2) | 0·097 (6) | 1·00 |
| O(5)5 | 0·7464 (2) | 0·1255 (2) | 0·3303 (2) | 0·111 (7) | 1·00 |
| O(6)5*A* | 0·7900 (6) | 0·0438 (4) | 0·4009 (4) | 0·19 (1) | 0·71 |
| O(6)5*B* | 0·695 (1) | 0·062 (1) | 0·421 (1) | 0·24 (1) | 0·29 |
| C(1)6 | 0·5574 (3) | 0·2857 (3) | 0·2819 (4) | 0·099 (8) | 1·00 |
| C(2)6 | 0·5990 (3) | 0·2888 (3) | 0·2308 (3) | 0·090 (8) | 1·00 |
| C(3)6 | 0·6277 (3) | 0·2356 (3) | 0·2196 (3) | 0·090 (8) | 1·00 |
| C(4)6 | 0·6569 (3) | 0·2178 (3) | 0·2755 (4) | 0·102 (9) | 1·00 |
| C(5)6 | 0·6127 (3) | 0·2118 (3) | 0·3238 (3) | 0·090 (8) | 1·00 |
| C(6)6 | 0·6376 (3) | 0·1950 (4) | 0·3813 (3) | 0·113 (9) | 1.00 |
| O(2)6 | 0·5677 (2) | 0·3091 (2) | 0·1816 (2) | 0·110 (6) | 1·00 |
| O(3)6 | 0·6685 (2) | 0·2419 (2) | 0·1742 (2) | 0·103 (6) | 1·00 |
| O(4)6 | 0·6834 (2) | 0·1634 (2) | 0·2642 (2) | 0·099 (6) | 1·00 |
| O(5)6 | 0·5866 (2) | 0·2641 (2) | 0·3306 (2) | 0·100 (6) | 1·00 |
| O(6)6 | 0·6766 (2) | 0·2340 (3) | 0·4016 (2) | 0·133 (7) | 1·00 |
| O*W*(1) | 0·6204 (3) | 0·3248 (3) | 0·4536 (3) | 0·165 (8) | 1·00 |
| O*W*(2) | 0·5856 (4) | 0·4053 (4) | 0·8389 (5) | 0·26 (1) | 1·00 |
| O*W*(3) | 0·5863 (6) | 0·4333 (5) | 0·6067 (5) | 0·32 (1) | 1·00 |
| O*W*(4) | 0·4263 (7) | 0·4244 (6) | 0·2922 (8) | 0·33 (1) | 0·82 |
| O*W*(5) | 0·5508 (6) | 0·3977 (6) | 1·0440 (6) | 0·35 (1) | 0·90 |
| O*W*(6) | 0·8161 (7) | 0·1439 (7) | 0·4599 (6) | 0·38 (1) | 0·86 |
| O*W*(7) | 0·8972 (8) | 0·0576 (8) | 0·3873 (9) | 0·44 (1) | 0·93 |
| O*W*(8) | 0·8796 (8) | 0·0786 (7) | 1·0616 (8) | 0·41 (1) | 0·85 |
| O*W*(9) | 0·4156 (5) | 0·4131 (4) | 0·8369 (7) | 0·27 (1) | 0·85 |
| O*W*(10) | 0·5427 (7) | 0·4223 (7) | 0·7141 (7) | 0·27 (1) | 0·64 |
| O*W*(11) | 0·408 (1) | 0·481 (1) | 0·448 (1) | 0·33 (1) | 0·50 |
| O*W*(12) | 0·500 (0) | 0·500 (0) | 0·122 (1) | 0·36 (1) | 0·34 |
| O*W*(13) | 0·643 (1) | 0·024 (1) | 0·785 (1) | 0·40 (1) | 0·61 |
| O*W*(14) | 0·586 (1) | 0·113 (1) | 0·7885 (9) | 0·34 (1) | 0·56 |
| O*W*(15) | 0·510 (2) | 0·079 (2) | 0·353 (2) | 0·39 (1) | 0·29 |
| O*W*(16) | 0·590 (1) | 0·085 (1) | 0·168 (1) | 0·38 (1) | 0·45 |
| O*W*(17) | 0·466 (2) | 0·059 (2) | 0·974 (1) | 0·32 (1) | 0·28 |
| O*W*(18) | 0·505 (3) | 0·116 (2) | 0·487 (3) | 0·25 (1) | 0·15 |
| O*W*(19) | 0·494 (2) | 0·130 (2) | 0·152 (2) | 0·38 (1) | 0·37 |
| O*W*(20) | 0·576 (2) | 0·075 (2) | 0·476 (1) | 0·35 (1) | 0·35 |

All calculations were performed on a MicroVAX 3500 computer. The structures were refined by the blocked full-matrix least-squares technique employing the program *SHELX*76 (Sheldrick, 1976). The minimizing function used was $\sum w(|F_o| - |F_c|)^2$ with unit weights $w = 1{\cdot}00$.

## Results and discussion

Owing to the better *R* factor to which the refinement of crystal (1) converged, the following discussion is based on the results for this sample. A comparison of crystal (2) with crystal (1) is given in the last section of this paper.

Final coordinates of non-H atoms and their equivalent isotropic temperature factors for crystal (1) with standard deviations are given in Table 2. The bond lengths and bond angles, the anisotropic temperature factors, and the coordinates of calculated H atoms are deposited in Tables 6–9.*

The atom numbering in the glucose residues is the same as used in our previous publications (see, for example, Noltemeyer & Saenger, 1980): C(5)2 means carbon atom 5 of glucose residue 2. The crystal

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* Lists of bond lengths, bond angles, torsion angles, tilt angles, puckering parameters, hydrogen bonds, structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54080 (170 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

asymmetric unit contains three pairs of glucose residues. Each of these pairs generates one complete $\gamma$-CD molecule by the $P4$ symmetry operation. $\gamma$-CD molecule $A$ is formed by glucose residues 1 and 2, molecule $B$ by residues 3 and 4, and molecule $C$ by residues 5 and 6.

### *Crystal packing*

The crystal packing is shown in Figs. 1 and 2. The $\gamma$-CD molecules are stacked on top of each other along the fourfold axes parallel to $c$. Their cavities form endless channels with a diameter of about 8 Å, in which the 1-propanol and 3·1 water molecules are accommodated, see Fig. 1. In the stack, $\gamma$-CD molecules $A$ and $C$ point in the same direction [O(2)/O(3) side 'up'], while molecule $B$ is oriented oppositely. This implies that all three possible arrangements, tail-to-tail ($A$ and $B$), head-to-head ($B$ and $C$) and tail-to-head ($C$ and $A$) are found for adjacent $\gamma$-CD molecules, where 'head' means the O(6) side and 'tail' the O(2) and O(3) side, see Fig. 3. Hydrogen bonds are formed between the O(2)/O(3) rims of $A$ and $B$, the O(6) rims of $B$ and $C$, and the O(2)/O(3) rim of $C$ and the O(6) rim of $A$. This arrangement of the $\gamma$-CD molecules in the stack is unique in CD structures, as in $\alpha$- and $\beta$-CD channel structures only the head-to-head (and tail-to-tail) or head-to-tail type arrangements were found. The stacks are related to each other by the twofold axis and the twofold screw axis. This results in a square packing of the stacks, see Fig. 2, with a solvent-filled interstitial 'minor' channel, with a diameter of about 7 Å. This arrangement of stacks is unusual; in $\alpha$- and $\beta$-CD channel structures the CD stacks are mostly packed in more or less hexagonal arrangements (see, for example, Saenger, 1984); a square packing has thus far only been observed in the $\alpha$-CD–$Cd_{0.5}I_5$–26$H_2O$ polyiodide complex (Noltemeyer & Saenger, 1980).

### *Conformation of the $\gamma$-CD molecules*

The conformation of the glucose residues and the orientation of the residues relative to each other are, as usually, described by a selection of endocyclic and exocyclic torsion angles, Table 3. The three $\gamma$-CD molecules are in a symmetrical and almost 'round' shape; this geometry is required by the crystallographic $P4$ symmetry. The C(4)—O(4)—(1)″ interglucose bond angles, Table 7 (deposited), range from 115·2 (6) to 117·9 (6)° with an average value of 116·8°. This value is little smaller than the $\beta$-CD value of 117·7° (Lindner & Saenger, 1982) and that of $\alpha$-CD at 119·0° (Hingerty & Saenger, 1976). It reflects the widening of the CD macrocycle from six to eight glucoses, which is accompanied by a reduction of curvature. The tilt angle between the O(4) plane and the least-squares planes through the atoms C(1), C(4), O(4) and O(4)′ have values between 11·8 and 18·0° with an average of 14·9°, see Table 4. This means that all residues are inclined with their O(6) side slightly turned to the inside of the macrocycle. The inclinations increase slightly in individual $\gamma$-CD molecules from $A$ to $C$; this may be caused by the intermolecular hydrogen bonds between $\gamma$-CD molecules. The spread of these values is much smaller than in the complex $\gamma$-CD–14$H_2O$, where the tilt angles range from $-2·5$ to 23·8° with an average of 13·9° (Harata, 1987), but is similar in the complex $\gamma$-CD–12-crown-4–NaCl, where the tilt angles are in the range 11·3 to 17·6° with an average value of 14·7° (Kamitori, Hirotsu & Higuchi, 1988).

All six glucose residues are in the usual $^4C_1$ chair conformation with some degree of flexibility, see Fig. 4. All endocyclic torsion angles are in the *gauche* range with deviations from the mean torsion angles less than ±2·5°. The Cremer and Pople ring-puckering parameters (Cremer & Pople, 1975) of the glucoses are in Table 10 (deposited). The variations in the total puckering amplitude $Q_T$ and the angular

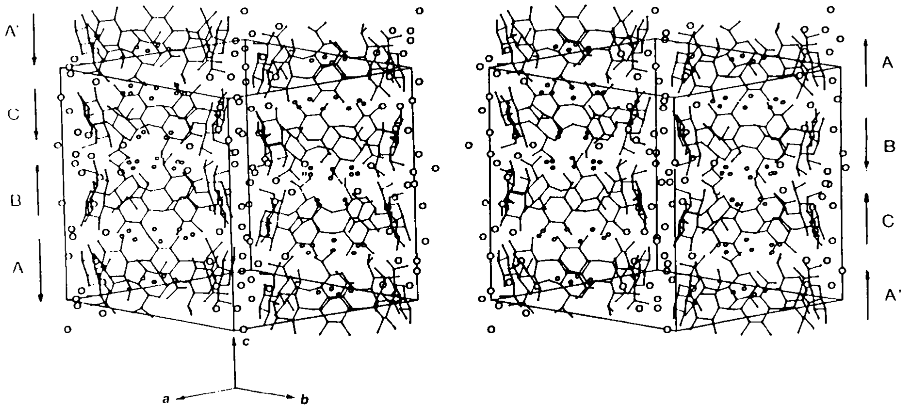

Fig. 1. Stereoview of the unit-cell contents for crystal (1), looking along [110]. Small circles: water molecules situated in the major $\gamma$-CD channels; large circles: water molecules situated in the minor interstitial channels.

variables $\theta_2$ and $\varphi_2$ indicate that there are slight distortions from ideal $^4C_1$ geometry.

The O(6) hydroxyl groups of glucoses 1 to 5 are twofold disordered. For the major occupation sites *A*, the torsion angles O(5)—C(5)—C(6)—O(6), which define the orientation of the C(6)—O(6) bond, are in the (−)*gauche* range, hence the C(6)—O(6) bonds point 'away' from the molecular axis; for the minor sites *B*, the C(6)—O(6) bond points 'inward' with torsion angle O(5)—C(5)—C(6)—O(6) in the (+)*gauche* range. A very unusual case is the minor site O(6)4*B*, occupancy = 0·31, with an O(5)—C(5)—C(6)—O(6) torsion angle of 4° in the *cis* range. This peculiar orientation for C(6)—O(6) is also observed in crystal (2), see Table 16 (deposited).

### *The solvent molecules*

In the crystal asymmetric unit, 12·8 water molecules are distributed over 20 sites (and there are 12·8 × 8/6 = 17·0H$_2$O per $\gamma$-CD molecule, as given in the title). The water molecules are located in the two channels. Since the 'major' channel formed by the $\gamma$-CD cavities has fourfold symmetry, the enclosed 1-propanol molecule is disordered. This leads to poorly characterized electron density which could be associated with statistical disorder, or with diffusive motions of the 1-propanol molecules within the channel. In the 'major' channel eight partially occupied water positions, O*W*(13) to O*W*(20) in Table 2, were identified; their occupancy factors are in the range 0·61 to 0·15 in crystal (1) and 0·54 to 0·14 in crystal (2); they sum up to 3·1. Water sites O*W*(15) (occupancy = 0·29) and O*W*(17) (occupancy = 0·28) are located within the central part of the $\gamma$-CD cavities and do not form hydrogen bonds to the macrocycles. The other water sites are placed in the planes of the hydroxyl rims of the macrocycles. Four of them [O*W*(16), O*W*(18), O*W*(19), O*W*(20)] form hydrogen bonds with O(6)*B* hydroxyl groups turned 'inward' (Fig. 3), and two of them [O*W*(13) and O*W*(14)] form hydrogen bonds only to each other. Hydrogen bonds between O(2), O(3) hydroxyl groups and enclosed water molecules are not observed. Extended maxima of electron density that appear to correspond to propanol molecules were found near or on the fourfold axis. Since atoms assigned to them could not be refined satisfactorily, the location of these molecules within the channel remains unclear.

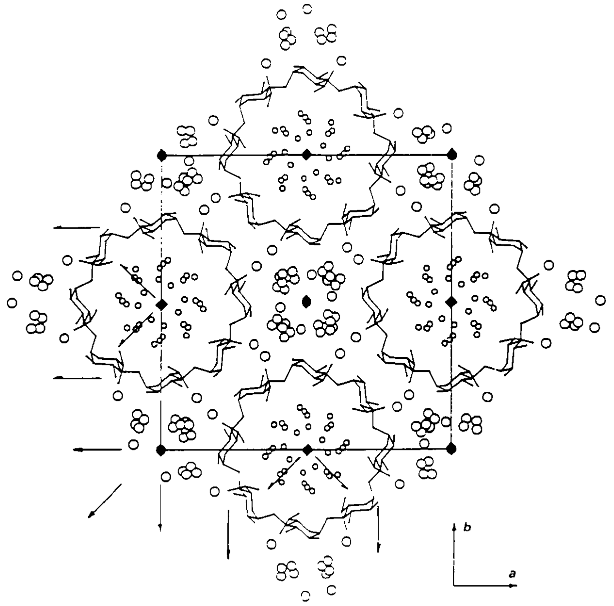

Fig. 2. View of the crystal structure looking down the *c* axis. Shown is $\gamma$-CD molecule *A* with water molecules for crystal (1). Small circles: water molecules located in the major $\gamma$-CD channels; large circles: water molecules located in the minor interstitial channels.

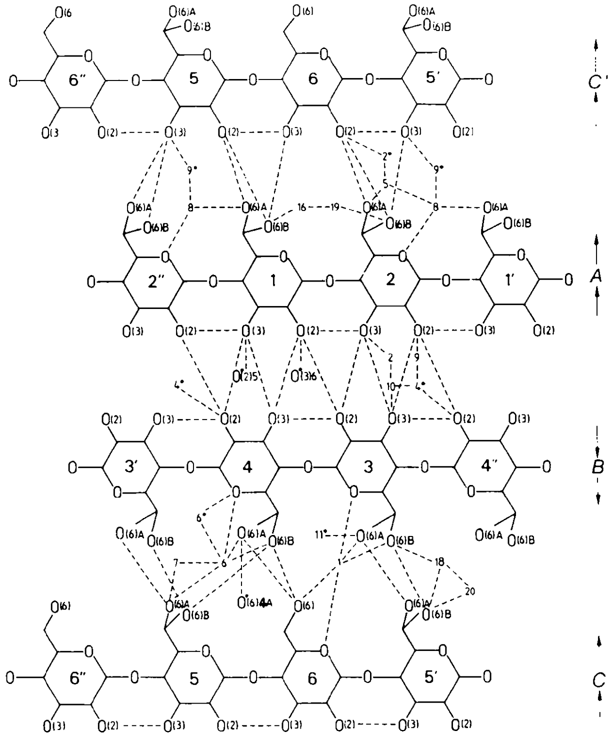

Fig. 3. Schematic representation of the hydrogen bonds involving $\gamma$-CD hydroxyl groups for crystal (1). O···O distances ≤ 3·4 Å, which we assign as hydrogen bonds, are indicated by dotted lines; water molecules are only given by their numbers; atoms related by symmetry are indicated by *. The inset numbers of the glucoses represent the residue unit numbers, the next 'higher' glucose units in the $\gamma$-CD ring are marked with ′ and the next 'lower' glucose units are marked with ″. The arrows indicate the polarity of $\gamma$-CD molecules, from O(2)/O(3) to O(6).

Table 3. *Selected torsion angles* (°) *for crystal* (1)

Standard deviations are given in parentheses. Atoms marked ′ belong to next higher glucose units. Atoms marked ″ belong to next lower glucose units.

| | Molecule *A* | | Molecule *B* | | Molecule *C* | |
|---|---|---|---|---|---|---|
| | *G*1 | *G*2 | *G*3 | *G*4 | *G*5 | *G*6 |
| C(1)—C(2)—C(3)—C(4) | −54·9 (8) | −55·3 (9) | −54·5 (8) | −55·5 (9) | −50·6 (9) | −56·0 (8) |
| C(2)—C(3)—C(4)—C(5) | 57·2 (8) | 56·6 (8) | 58·7 (8) | 54·1 (8) | 53·7 (9) | 58·7 (8) |
| C(3)—C(4)—C(5)—O(5) | −57·7 (8) | −56·1 (8) | −59·8 (8) | −53·9 (9) | −55·8 (9) | −59·7 (8) |
| C(4)—C(5)—O(5)—C(1) | 60·3 (8) | 58·5 (8) | 61·4 (8) | 55·7 (9) | 60·8 (9) | 61·0 (8) |
| C(5)—O(5)—C(1)—C(2) | −60·8 (8) | −57·0 (8) | −57·6 (8) | −53·7 (9) | −59·2 (9) | −56·4 (8) |
| O(5)—C(1)—C(2)—C(3) | 54·7 (8) | 52·9 (8) | 53·8 (9) | 53·8 (9) | 52·0 (9) | 53·1 (8) |
| O(5)—C(5)—C(6)—O(6)*A* | −68·1 (9) | −69·7 (9) | −56·4 (9) | −62 (1) | −59 (1) | −59·3 (8) |
| O(5)—C(5)—C(6)—O(6)*B* | 67 (1) | 61 (1) | 46 (2) | 4 (1) | 65 (2) | |
| O(2)—C(2)—C(3)—O(3) | 64·9 (7) | 62·7 (8) | 62·1 (8) | 57·4 (9) | 61·8 (8) | 62·1 (8) |
| C(3)—C(4)—O(4)—C(1)″ | 126·2 (7) | 126·8 (7) | 129·8 (7) | 128·4 (7) | 126·3 (7) | 131·4 (7) |
| C(5)—C(4)—O(4)—C(1)″ | −115·3 (7) | −111·7 (7) | −113·7 (7) | −109·3 (7) | −110·8 (7) | −110·0 (7) |
| O(5)—C(1)—O(4)′—C(4)′ | 110·1 (7) | 111·9 (7) | 107·5 (7) | 108·9 (7) | 107·3 (7) | 108·3 (7) |
| C(2)—C(1)—O(4)′—C(4)′ | −125·1 (7) | −130·3 (7) | −128·7 (7) | −131·7 (7) | −130·6 (7) | −134·8 (7) |

Table 4. *Tilt angles* (°) *for crystal* (1)

The tilt angle is defined as the angle between the plane through the O(4) atoms and the least-squares plane through C(1), C(4), O(4) and O(4)′ of each residue.

| Residue | Tilt angle | Residue | Tilt angle |
|---|---|---|---|
| *G*1 | 13·2 | *G*2 | 11·8 |
| *G*3 | 15·0 | *G*5 | 14·9 |
| *G*3 | 18·0 | *G*6 | 16·4 |

Table 5. *Hydrogen-bond distances* (Å) *for crystal* (1)

O···O distances ≤ 3·4 Å are given.

| O(I)···O(II) | Distance | Symmetry |
|---|---|---|
| O(2)1···O(3)2 | 2·750 | *x*, *y*, *z* |
| O(2)1···O(2)3 | 2·968 | *x*, *y*, *z* |
| O(2)1···O(3)4 | 3·212 | *x*, *y*, *z* |
| O(2)1···O(3)6 | 2·721 | 1 − *y*, 1 − *x*, 1 − *z* |
| O(3)1···O(2)2 | 2·773 | 0·5 − *y*, *x* − 0·5, *z* |
| O(3)1···O(2)4 | 3·211 | *x*, *y*, *z* |
| O(3)1···O(3)4 | 2·791 | *x*, *y*, *z* |
| O(3)1···O(2)5 | 2·816 | 1 − *y*, 1 − *x*, 1 − *z* |
| O(6)1*A*···O(2)5 | 2·768 | *x*, *y*, *z* − 1 |
| O(6)1*A*···O*W*(8) | 2·974 | *x*, *y*, *z* |
| O(6)1*B*···O(2)5 | 3·154 | *x*, *y*, *z* − 1 |
| O(6)1*B*···O(3)6 | 3·066 | *x*, *y*, *z* − 1 |
| O(6)1*B*···O*W*(16) | 2·784 | *x*, *y*, *z* − 1 |
| O(2)2···O(3)3 | 3·177 | *x*, *y*, *z* |
| O(2)2···O(2)4 | 2·985 | 0·5 + *y*, 0·5 − *x*, *z* |
| O(2)2···O*W*(9) | 2·730 | *x*, *y*, *z* |
| O(3)2···O(2)3 | 3·182 | *x*, *y*, *z* |
| O(3)2···O(3)3 | 2·843 | *x*, *y*, *z* |
| O(3)2···O*W*(2) | 2·912 | *x*, *y*, *z* |
| O(5)2···O*W*(8) | 3·142 | 0·5 + *y*, 0·5 − *x*, *z* |
| O(6)2*A*···O(2)6 | 2·869 | *x*, *y*, *z* − 1 |
| O(6)2*A*···O*W*(5) | 2·790 | *x*, *y*, *z* |
| O(6)2*B*···O(3)5 | 3·248 | 0·5 + *y*, 0·5 − *x*, *z* − 1 |
| O(6)2*B*···O(2)6 | 3·125 | *x*, *y*, *z* − 1 |
| O(6)2*B*···O*W*(19) | 2·592 | *x*, *y*, *z* − 1 |
| O(2)3···O(3)4 | 2·832 | *x*, *y*, *z* |
| O(3)3···O(2)4 | 2·866 | 0·5 + *y*, 0·5 − *x*, *z* |
| O(3)3···O*W*(10) | 3·115 | *x*, *y*, *z* |
| O(5)3···O*W*(1) | 3·320 | *x*, *y*, *z* |
| O(6)3*A*···O(6)5*A* | 2·838 | 0·5 + *y*, 0·5 − *x*, *z* |
| O(6)3*A*···O*W*(1) | 2·815 | *x*, *y*, *z* |
| O(6)3*A*···O*W*(11) | 3·001 | *y*, *x*, 1 − *z* |
| O(6)3*B*···O(6)5*B* | 3·234 | 0·5 + *y*, 0·5 − *x*, *z* |
| O(6)3*B*···O*W*(1) | 2·957 | *x*, *y*, *z* |
| O(6)3*B*···O*W*(18) | 2·849 | *x*, *y*, *z* |
| O(2)4···O*W*(4) | 3·074 | *x* − 0·5, 0·5 − *y*, 1 − *z* |
| O(5)4···O*W*(6) | 3·194 | *x*, *y*, *z* |
| O(5)4···O*W*(6) | 3·098 | 1 − *y*, 1 − *x*, 1 − *z* |
| O(6)4*A*···O(6)4*A* | 3·007 | 1 − *y*, 1 − *x*, 1 − *z* |
| O(6)4*A*···O(6)6 | 2·866 | *x*, *y*, *z* |
| O(6)4*A*···O*W*(6) | 2·857 | *x*, *y*, *z* |
| O(6)4*B*···O(6)5*B* | 2·371 | *x*, *y*, *z* |
| O(6)4*B*···O(6)6 | 3·024 | *x*, *y*, *z* |
| O(6)4*B*···O*W*(6) | 2·447 | *x*, *y*, *z* |
| O(2)5···O(3)6 | 2·908 | *x*, *y*, *z* |
| O(3)5···O(2)6 | 2·837 | 0·5 − *y*, *x* − 0·5, *z* |
| O(3)5···O*W*(9) | 2·986 | *x* − 0·5, 0·5 − *y*, 1 − *z* |
| O(6)5*A*···O*W*(6) | 2·821 | *x*, *y*, *z* |

For the interstitial 'minor' channel between the stacks of $\gamma$-CD molecules (with a diameter of about 7 Å) the interpretation of electron density is less ambiguous. Unlike the main channel with predominantly hydrophobic walls, its surface is formed by the outsides of $\gamma$-CD molecules and offers numerous primary and secondary hydroxyl groups for hydrogen bonding. Twelve water positions, O*W*(1) to O*W*(12), were located within this region, only two of them [O*W*(3) and O*W*(12)] not forming direct hydrogen bonds with $\gamma$-CD hydroxyl groups (Fig. 3). The occupany factors sum up to 9·7 for all twelve positions; three positions are fully occupied. The solvent arrangement near the twofold axis running along the center of this channel, see Fig. 2, is still unclear. No electron density corresponding to the size of propanol molecules could, however, be observed in this channel.

### *Hydrogen bonds*

The crystal structure displays an intricate network of interconnected hydrogen bonds. All O···O distances shorter than 3·4 Å, which are suggestive of hydrogen bonds, are listed in Table 5, and a schematic representation of the hydrogen-bonding pattern is drawn in Fig. 3.

A ring of intramolecular interglucose O(2)···O(3)′ hydrogen bonds, which stabilizes the 'round' struc-

Table 5 (*cont.*)

| O(I)···O(II) | Distance | Symmetry |
|---|---|---|
| O(6)5*A*···O*W*(7) | 2·594 | *x*, *y*, *z* |
| O(6)5*B*···O*W*(18) | 2·921 | 0·5 + *y*, 0·5 − *x*, *z* |
| O(6)5*B*···O*W*(20) | 3·126 | *x*, *y*, *z* |
| O(2)6···O*W*(2) | 2·634 | 1 − *y*, 1 − *x*, 1 − *z* |
| O(5)6···O*W*(1) | 3·303 | *x*, *y*, *z* |
| O(6)6···O*W*(1) | 2·819 | *x*, *y*, *z* |
| O*W*(1)···O*W*(1) | 2·841 | 1 − *y*, 1 − *x*, 1 − *z* |
| O*W*(1)···O*W*(3) | 2·846 | 1 − *y*, 1 − *x*, 1 − *z* |
| O*W*(2)···O*W*(5) | 2·939 | 1 − *y*, 1 − *x*, 2 − *z* |
| O*W*(2)···O*W*(10) | 3·101 | *x*, *y*, *z* |
| O*W*(2)···O*W*(12) | 3·175 | *y*, *x*, 1 − *z* |
| O*W*(2)···O*W*(12) | 3·175 | 1 − *y*, 1 − *x*, 1 − *z* |
| O*W*(3)···O*W*(7) | 2·996 | 1·5 − *x*, *y* − 0·5, 1 − *z* |
| O*W*(3)···O*W*(10) | 2·716 | *x*, *y*, *z* |
| O*W*(3)···O*W*(11) | 2·871 | *y*, *x*, 1 − *z* |
| O*W*(4)··O*W*(7) | 2·334 | 0·5 + *y*, 0·5 − *x*, *z* |
| O*W*(4)···O*W*(9) | 3·022 | *y*, *x*, 1 − *z* |
| O*W*(4)···O*W*(10) | 2·826 | *y*, *x*, 1 − *z* |
| O*W*(5)···O*W*(5) | 2·686 | 1 − *y*, 1 − *x*, 2 − *z* |
| O*W*(5)···O*W*(8) | 3·140 | 0·5 + *y*, 0·5 − *x*, *z* |
| O*W*(5)···O*W*(12) | 3·270 | *x*, *y*, *z* − 1 |
| O*W*(5)···O*W*(12) | 3·270 | 1 − *x*, 1 − *y*, *z* − 1 |
| O*W*(6)···O*W*(6) | 2·302 | 1 − *y*, 1 − *x*, 1 − *z* |
| O*W*(6)···O*W*(7) | 3·287 | *x*, *y*, *z* |
| O*W*(7)···O*W*(11) | 2·585 | 0·5 − *y*, *x* − 0·5, *z* |
| O*W*(8)···O*W*(8) | 3·187 | 1 − *y*, 1 − *x*, 2 − *z* |
| O*W*(8)···O*W*(9) | 2·520 | *x* + 0·5, 0·5 − *y*, 2 − *z* |
| O*W*(9)···O*W*(12) | 3·041 | *y*, *x*, 1 − *z* |
| O*W*(9)···O*W*(12) | 3·041 | 1 − *y*, 1 − *x*, 1 − *z* |
| O*W*(13)···O*W*(14) | 2·516 | *x*, *y*, *z* |
| O*W*(13)···O*W*(14) | 2·709 | 0·5 − *y*, *x* − 0·5, *z* |
| O*W*(15)···O*W*(15) | 2·684 | 0·5 − *y*, *x* − 0·5, *z* |
| O*W*(15)···O*W*(15) | 2·684 | 0·5 + *y*, 0·5 − *x*, *z* |
| O*W*(15)···O*W*(18) | 3·258 | *x*, *y*, *z* |
| O*W*(15)···O*W*(20) | 3·238 | *x*, *y*, *z* |
| O*W*(16)···O*W*(19) | 2·556 | *x*, *y*, *z* |
| O*W*(16)···O*W*(19) | 2·145 | 0·5 − *y*, *x* − 0·5, *z* |
| O*W*(17)···O*W*(17) | 3·216 | 1 − *x*, − *y*, *z* |
| O*W*(17)···O*W*(17) | 2·274 | 0·5 − *y*, *x* − 0·5, *z* |
| O*W*(17)···O*W*(17) | 2·274 | 0·5 + *y*, 0·5 − *x*, *z* |
| O*W*(18)···O*W*(20) | 1·970 | *x*, *y*, *z* |
| O*W*(18)···O*W*(20) | 2·149 | 0·5 + *y*, 0·5 − *x*, *z* |

ture of $\gamma$-CD, is observed for all three $\gamma$-CD molecules in this crystal. The mean O(2)···O(3)′ distance is 2·83 Å. In the isomorphous complex $\gamma$-CD–12-crown-4–NaCl, an average O(2)···O(3)′ distance of 2·86 Å is observed (Kamitori, Hirotsu & Higuchi, 1988), in $\gamma$-CD–14$H_2O$ this mean distance is 2·82 Å (Harata, 1987). These values are nearly the same as for $\beta$-CD [for example, 2·86 Å (Lindner & Saenger, 1982), 2·83 Å (Hamilton & Chen, 1988), 2·78 Å (Jogun, 1979)], where a similar ring of O(2)···O(3)′ hydrogen bonds has been observed in all crystal structures published until now. This observation contradicts the statement that these intramolecular hydrogen bonds in $\gamma$-CD are stronger than in $\beta$-CD (Harata, 1987). In $\alpha$-CD, the O(2)···O(3)′ hydrogen bonds are significantly longer, and consequently weaker, with an average distance of 3·00 Å (Saenger, 1980). This is corroborated by spectrosopic data which showed a decreased macrocycle stability of $\alpha$-CD relative to $\beta$- and $\gamma$-CD (Hingerty & Saenger, 1976; Rees, 1970), and led to the 'induced fit' hypothesis for inclusion formation of $\alpha$-CD (Saenger, 1984).

$\gamma$-CD molecules *A* and *B* touch with their O(2)/O(3) rims ('tail-to-tail' arrangement). A regular pattern of hydrogen bonds is formed between these secondary hydroxyl groups, see Fig. 3. This pattern is practically the same as the one found in tail-to-tail dimers of $\beta$-CD molecules (see, for example, Jogun, 1979; Hamilton & Chen, 1988; Steiner, Hinrichs & Saenger, 1989), where, however, the regularity is always less perfect.

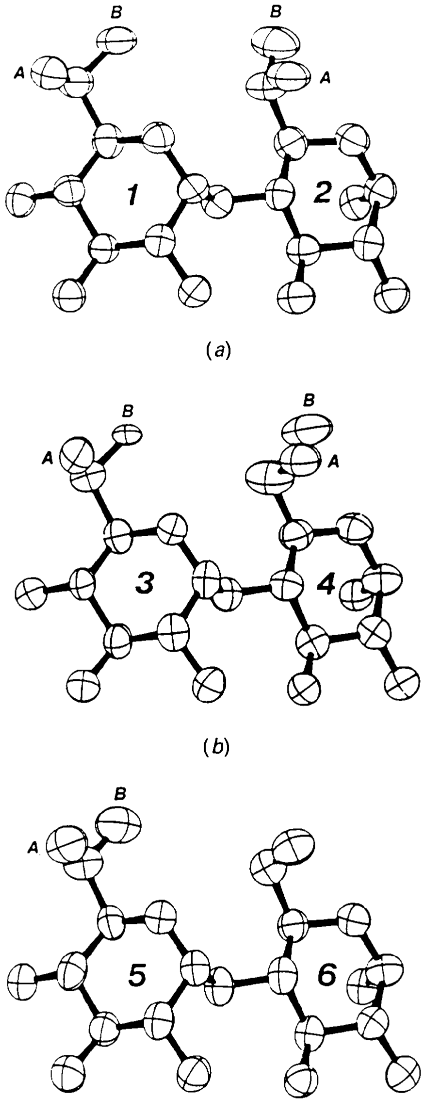

Fig. 4. Views of the molecular structures for crystal (1) (30% thermal probability ellipsoids for all atoms). (*a*) Glucose residues 1 and 2 ($\gamma$-CD molecule *A*); (*b*) glucose residues 3 and 4 ($\gamma$-CD molecule *B*); (*c*) glucose residues 5 and 6 ($\gamma$-CD molecule *C*).

γ-CD molecules *A* and *C* interact with the O(6) rim of *A* and the O(2)/O(3) rim of *C* ('head-to-tail' arrangement). All O(6) and O(2)/O(3) hydroxyl groups are engaged in hydrogen bonds with the neighboring molecule. For molecule *A*, the primary hydroxyls form hydrogen bonds to O(2) hydroxyls of *C* in their major site O(6)*A* and to O(2) and O(3) hydroxyls in the minor site O(6)*B*.

γ-CD molecules *B* and *C* interact with their O(6) rims ('head-to-head' arrangement). The O(6) hydroxyl groups take part in hydrogen bonding in any of their positions, but the resulting pattern between the rims is irregular, see Fig. 3.

As a result of the square arrangement, the γ-CD stacks are not in close (hexagonal) packing, and consequently there is little hydrogen-bonding contact between them. Only two hydrogen bonds from one stack to another, O(3)1···O(2)5 and O(2)1···O(3)6, are observed.

While the hydrogen-bonding situation in the 'major' channel remains unclear, most of the water molecules in the 'minor' interstitial channel are part of a well defined hydrogen-bonding network, see Fig. 3.

### *Comparison between crystal* (1) *and crystal* (2)

All results for crystal (2) are deposited in Tables 11 to 19.* As expected, they are practically identical for both crystals. This holds even for the orientations and occupancies of the disordered O(6) hydroxyl groups, and the positions and occupancies of most of the disordered water molecules. However, there are still some subtle differences in the site-occupancy factors of water molecules (Tables 2 and 11) and especially if the hydrogen-bonding schemes (Tables 5 and 19) are compared. There is one interaction between O(6) minor sites occurring only in crystal (1), O(6)3*B*···O(6)5*B*, 3·234 Å, and all the other hydrogen-bonding distances that are in variance involve water molecules: the interactions O(6)2*B*···O*W*(19), 2·592; O(6)5*B*···O*W*(18), 2·921; O(6)5*B*···O*W*(20), 3·126; O*W*(3)···O*W*(11), 2·871; O*W*(5)···O*W*(12), 3·270; O*W*(15)···O*W*(15), 2·684; O*W*(15)···O*W*(18), 3·258; O*W*(15)···O*W*(20), 3·238 Å are only observed in crystal (1). In crystal (2), there are the following interactions that are not observed in crystal (1): O(2)5···O*W*(5), 3·287; O*W*(11)···O*W*(11), 2·968; O*W*(20)···O*W*(20), 1·924 and 2·721 Å. Most of the atomic sites involved in these interactions are occupied to the extent of less than 0·5 [and therefore the short O*W*(20)···O*W*(20) distance, 1·924 Å, is acceptable], with the exceptions O(2)5···O*W*(5)(0·96), and O*W*(11)···O*W*(11)(0·67). Since both crystal structures were determined at high resolution and refined to comparable accuracy, artifacts resulting from data collection, refinement or interpretation appear improbable. Consequently, the two crystals are different, in their water structure, with the low-occupancy water sites more strongly affected than those with high occupancy.

That crystals from different batches show differences in their hydration has previously been observed with β-CD (Fujiwara *et al.*, 1983; Steiner, 1990). Since predominantly low-occupancy sites are involved, the differences are not easily detectable in X-ray diffraction photographs and it is necessary to determine the structures at high resolution to really see them.

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* See deposition footnote.

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