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X-ray crystallographic structure of the two-to-one α-cyclodextrin-acetone. $9H_2O$ compound

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An inclusion complex of acetone with α-cyclodextrin (α-CD) has been prepared in aqueous solution containing AG^+ ions. The crystal structure of the complex has been determined by single crystal X-ray diffraction. Crystal data: triclinic, space group $P1$, $Z=1$, a = 13.852(1), b = 13.878(1), c = 15.719(1) Å, $\alpha = 93.01(1)$, $\beta = 91.98(1)$, $\gamma = 119.32(1)°$ and $R = 0.069$ for 6092 observed MoKα reflections with $I > 3\sigma(I)$. This crystalline form is of the dimeric-type structure which normally occurs for ionic guest molecules. The dimers are stacked along the c axis to form an 'endless head-to-head' channel. Nine water molecules fill the intermolecular space outside the dimeric cavity and contribute to reinforce the cohesion between the channels which are in a pseudo-hexagonal arrangement. The acetone molecule is encapsulated within the cavity of the dimer. Molecular graphics analysis of difference Fourier maps suggests that the acetone molecule is situated in several partially occupied sites forming an infinite chain lying along the dimer axis. Thus, the stoichiometry for the complex corresponds to 2 α-CD molecules per acetone molecule, but this is not a true 2:1 inclusion compound.

INTRODUCTION

α-Cyclodextrin (α-CD) crystallizes essentially as monomeric units in either a cage-type structure for small, non-ionic guest molecules or an 'endless head-to-tail' channel type structure for long or ionic guest molecules.[1–3] All these structures are concerned with (1-1) complexes. Dimeric-type structures, less frequent, are only obtained with ionic guest complexes: polyiodides with a variety of cations[4] and transition-metal[5–7] complexes. This third class of structures is characterized by a packing of dimers of α-CD in an 'endless head-to-head' channel. We report here the first example of a crystalline form of a dimeric non-ionic (2-1) α-CD complex obtained, surprisingly, by crystallization from aqueous solutions containing monovalent cations.

The title compound was prepared in the hope of realising α-CD complexes with Ag^+ ions, but the structure does not reveal the presence of a cation site, although belonging to the third class of structure, isomorphous to the pseudo hexagonal triclinic forms which have been only observed with monovalent cations.

EXPERIMENTAL

Preparation of crystalline complexes

An aqueous solution containing 1:1 equivalence of α-CD and $AgNO_3$ was prepared (10 mL, 0.2 M in both components). At the surface of this solution was layered 5 mL of acetone and the tube stoppered to allow diffusion of the acetone into the aqueous solution. After 1 day, a dark coloured precipitate was observed, and after 3 days very small colourless crystals of the title compound were observed. The crystals were left to grow during 3 months, at which point suitable crystals for X-ray crystallography were removed from the solution.

X-ray structural analysis

Single crystals of the complex were sealed, in the presence of the mother liquor, in thin glass capillaries, tested by photographic methods, and then mounted on an Enraf-Nonius CAD-4 diffractometer. Cell constants were determined from setting angles of 25 reflections in the range $9° < \theta < 37°$. Crystallographic data is summarized in Table 1.

The structure was solved starting from positional parameters of α-CD in the related structure[4] of the complex $(\alpha\text{-CD})_2.Li^+.I_3^-.I_2$, $8H_2O$. Due to the large

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Table 1 Crystallographic data collection and structure refinement

Crystal colour	Colourless
Crystal size (mm)	0.20 × 0.20 × 0.60
$\mu(CuK_\alpha)$, cm^{-1}	11.7—no correction
Corrections	Background, Lorentz Polarization, Decay, Absorption
Space Group	P1
a (Å)	13.852 (1)
b (Å)	13.878 (1)
c (Å)	15.719 (1)
α (°)	93.01 (1)
β (°)	91.98 (1)
γ (°)	119.32 (1)
V ($Å^3$)	2624.7 (3)
Z	1
Diffractometer	CAD4
Monochromator	Graphite
Radiation	CuK_α ($\lambda = 1.54184$ Å)
Temperature (°C)	RT (room temperature)
Scan type	$\omega/2\theta$
Scan range (°)	$1.0 + 0.35 \tan\theta$
2θ range (°)	6–110
Scan speed	depending upon reflection
Standard reflections	$\bar{3}06$, $\bar{1}\bar{3}5$, $4\bar{2}\bar{5}$; measured every other hour
Reflections measured	4 octants, hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$
Reflections collected	6883
Unique reflections	6585
Reflections kept for refinement ($I > 3\sigma(I)$)	6092
Computing programs	SDP [8], SHELX-76 [9]
Atomic form factors	International Tables (vol. 4) [10]
Minimized function	$Sw(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Weighting scheme	$w = 7.221/(\sigma^2(F) + 0.00117F^2)$
Maximum shift/e.s.d.	2.2
No. of reflection/No. of parameters varied	7.0
No. of parameters	873
R	0.069
Rw	0.074
S	6.22

number of parameters to be refined only hydroxyl oxygen atoms were given anisotropic temperature factors, and H atoms bonded to C atoms were introduced in ideal positions, not refined. Two block matrices were used in the least-squares minimization of $\sum w(\Delta F)^2$. All calculations were performed on a Digital Micro Vax computer. In the last stages of the refinement it appeared that residual electron density peaks were located within the cavity of the dimer but not easily interpretable. A detailed analysis of the difference Fourier maps by means of molecular graphics led us to determine several partially occupied sites for acetone. Final atomic coordinates and thermal parameters of the non-hydrogen atoms are given in Table 2.

Molecular graphics

Analyses of the difference Fourier maps were carried out using the program FRODO[11] implemented on an Evans and Sutherland PS 330 interactive graphics Station piloted by a Microvax computer. Molecular graphics have been performed by the SYBYL programs package.[12]

DISCUSSION

The crystal structure consists of 'head-to-head' arranged dimers of α-CD molecules (Fig 1) which are stacked along the **c** axis forming 'endless' parallel channels in an pseudo-hexagonal dense packing (Fig 2). The structure reveals that one acetone molecule per two α-CD molecules is trapped within the cavity of the dimer on several partially occupied sites.

The overall packing of the structure is quite similar to those of the triclinic forms previously reported,[4-7] the matrix consisting of 2 α-CD molecules and 8 water molecules. Here, there is a new water molecule site and the hydrogen bonding scheme presents significant distortions at the secondary hydroxyl faces whereas it is undisturbed for the primary hydroxyl faces.

Table 2 Fractional coordinates (× 10^4) and isotropic or equivalent thermal parameters (× 10^3) of the atoms

	x	*y*	*z*	$U_{(\mathrm{iso/eq})}$
CD: Molecule A				
O(41A)	3208 (4)	3186 (4)	355 (3)	34 (1)
O(21A)	4814 (6)	1277 (6)	1733 (4)	152 (13)*
O(31A)	4835 (7)	3350 (5)	1684 (4)	73 (13)*
O(51A)	4257 (4)	1388 (4)	−524 (3)	36 (1)
C(11A)	4218 (7)	855 (7)	231 (5)	33 (2)
C(21A)	4798 (7)	1771 (7)	953 (5)	37 (2)
C(31A)	4209 (7)	2431 (7)	1074 (5)	35 (2)
C(41A)	4024 (6)	2847 (6)	228 (5)	31 (2)
C(51A)	3597 (7)	1927 (6)	−508 (5)	33 (2)
C(61A)	3690 (8)	2373 (7)	−1393 (6)	46 (2)
O(61A)	4764 (5)	3273 (5)	−1501 (4)	106 (12)*
O(42A)	3121 (5)	148 (5)	412 (3)	40 (1)
O(22A)	787 (5)	−3173 (6)	1731 (4)	85 (12)*
O(32A)	2745 (6)	−1014 (6)	1878 (4)	65 (14)*
O(52A)	1505 (5)	−2753 (5)	−483 (4)	43 (1)
C(12A)	814 (7)	−3205 (7)	216 (5)	37 (2)
C(22A)	1507 (7)	−2714 (7)	1043 (5)	43 (2)
C(32A)	2037 (7)	−1479 (7)	1099 (5)	41 (2)
C(42A)	2740 (7)	−1010 (7)	338 (5)	35 (2)
C(52A)	1981 (7)	−1582 (7)	−476 (5)	36 (2)
C(62A)	2563 (8)	−1247 (8)	−1316 (6)	46 (2)
O(62A)	3483 (5)	−1424 (5)	−1350 (4)	88 (12)*
O(43A)	−47 (4)	−2967 (4)	190 (3)	36 (1)
O(23A)	−3807 (5)	−4587 (5)	993 (4)	99 (11)*
O(33A)	−1548 (6)	−4132 (7)	1410 (4)	168 (15)*
O(53A)	−2702 (4)	−4308 (4)	−1111 (3)	35 (1)
C(13A)	−3342 (6)	−4205 (6)	−465 (5)	30 (2)
C(23A)	−3078 (6)	−4576 (7)	368 (5)	35 (2)
C(33A)	−1867 (7)	−3816 (7)	656 (5)	36 (2)
C(43A)	−1154 (6)	−3840 (6)	−58 (5)	29 (2)
C(53A)	−1523 (6)	−3640 (6)	−926 (5)	32 (2)
C(63A)	−1009 (7)	−3931 (7)	−1647 (5)	38 (2)
O(63A)	−1253 (5)	−5062 (5)	−1625 (4)	98 (12)*
O(44A)	−3078 (4)	−3096 (4)	−307 (3)	35 (1)
O(24A)	−4641 (5)	−931 (5)	823 (3)	90 (11)*
O(34A)	−4447 (5)	−2940 (5)	915 (4)	100 (11)*
O(54A)	−4143 (5)	−1485 (4)	−1366 (3)	38 (1)
C(14A)	−4107 (6)	831 (6)	−645 (5)	31 (2)
C(24A)	−4608 (7)	−1574 (7)	104 (5)	34 (2)
C(34A)	−3941 (6)	−2134 (6)	301 (5)	31 (2)
C(44A)	−3887 (6)	−2776 (6)	−505 (4)	27 (2)
C(54A)	−3531 (7)	−2052 (7)	−1258 (5)	35 (2)
C(64A)	−3683 (9)	−2723 (9)	−2079 (6)	56 (3)
O(64A)	−4819 (8)	−3466 (7)	−2293 (5)	118 (18)*
O(45A)	−3015 (4)	−24 (4)	−363 (3)	32 (1)
O(25A)	−1019 (5)	3727 (5)	912 (4)	58 (11)*
O(35A)	−2975 (4)	1487 (5)	901 (4)	58 (10)*
O(55A)	−1294 (5)	2621 (5)	−1284 (3)	38 (1)
C(15A)	−739 (7)	3291 (7)	−516 (5)	34 (2)
C(25A)	−1591 (7)	3015 (7)	155 (5)	37 (2)
C(35A)	−2118 (7)	1804 (6)	308 (5)	33 (2)
C(45A)	−2648 (6)	1096 (6)	−528 (4)	28 (2)
C(55A)	−1828 (7)	1440 (7)	−1213 (5)	37 (2)
C(65A)	−2346 (8)	929 (8)	−2091 (6)	48 (2)
O(65A)	−3188 (6)	1170 (6)	−2339 (4)	74 (12)*
O(46A)	80 (4)	3055 (4)	−191 (3)	34 (1)
O(26A)	3412 (5)	4827 (5)	1601 (3)	54 (11)*
O(36A)	1297 (5)	4647 (5)	1241 (4)	108 (12)*
O(56A)	2976 (4)	4193 (4)	−705 (3)	34 (1)
C(16A)	3456 (7)	4230 (7)	124 (5)	35 (2)
C(26A)	2971 (7)	4733 (7)	755 (5)	35 (2)
C(36A)	1712 (6)	4058 (6)	701 (5)	33 (2)
C(46A)	1217 (6)	3882 (6)	−189 (4)	28 (2)
C(56A)	1789 (6)	3464 (7)	−808 (5)	31 (2)
C(66A)	1420 (8)	3429 (8)	−1736 (5)	45 (2)
O(66A)	1483 (6)	4432 (6)	−1942 (4)	99 (13)*
CD: Molecule B				
O(41B)	−426 (4)	−3592 (4)	4634 (3)	36 (1)
O(21B)	3138 (5)	−1794 (5)	3458 (4)	102 (12)*
O(31B)	937 (5)	−3761 (5)	3372 (4)	73 (11)*
O(51B)	2367 (5)	−1806 (5)	5645 (3)	41 (1)
C(11B)	2894 (7)	−1354 (7)	4891 (5)	38 (2)
C(21B)	2531 (7)	−2264 (7)	4177 (5)	39 (2)
C(31B)	1320 (7)	−2822 (7)	3997 (5)	39 (2)
C(41B)	706 (6)	−3273 (6)	4805 (4)	31 (2)
C(51B)	1173 (7)	−2345 (7)	5538 (5)	37 (2)
C(61B)	777 (8)	−2809 (8)	6392 (6)	52 (2)
O(61B)	1139 (6)	−3537 (7)	6600 (5)	130 (14)*
O(42B)	2628 (4)	−550 (4)	4613 (3)	38 (1)
O(22B)	4135 (6)	2847 (6)	3297 (5)	210 (15)*
O(32B)	4094 (6)	716 (6)	3385 (4)	150 (13)*
O(52B)	3685 (4)	2301 (4)	5515 (3)	39 (1)
C(12B)	3661 (7)	2757 (7)	4734 (5)	35 (2)
C(22B)	4188 (8)	2367 (7)	4061 (5)	47 (2)
C(32B)	3524 (7)	1112 (6)	3928 (5)	37 (2)
C(42B)	3434 (7)	584 (6)	4760 (5)	33 (2)
C(52B)	3037 (7)	1114 (6)	5466 (5)	33 (2)
C(62B)	3142 (7)	796 (8)	6350 (6)	47 (2)
O(62B)	4249 (6)	1097 (6)	6585 (4)	90 (14)*
O(43B)	2575 (4)	2433 (4)	4439 (3)	35 (1)
O(23B)	471 (5)	3497 (6)	2630 (4)	123 (13)*
O(33B)	2534 (6)	3419 (6)	2885 (4)	175 (14)*
O(53B)	918 (4)	3766 (4)	4947 (3)	38 (1)
C(13B)	327 (6)	3514 (6)	4142 (5)	34 (2)
C(23B)	1128 (7)	3784 (7)	3434 (5)	42 (2)
C(33B)	1702 (7)	3091 (7)	3491 (5)	39 (2)
C(43B)	2231 (6)	3240 (6)	4388 (5)	32 (2)
C(53B)	1401 (6)	3055 (6)	5061 (5)	33 (2)
C(63B)	1912 (8)	3288 (8)	5975 (6)	48 (2)
O(63B)	2897 (6)	4342 (6)	6081 (5)	64 (14)*
O(44B)	−497 (4)	2413 (4)	4027 (3)	33 (1)
O(24B)	−4022 (4)	265 (5)	2502 (3)	50 (10)*
O(34B)	−1876 (5)	2170 (5)	2531 (3)	70 (10)*
O(54B)	−3289 (4)	974 (4)	4784 (3)	34 (1)
C(14B)	−3834 (6)	260 (6)	4029 (4)	27 (2)
C(24B)	−3468 (6)	953 (6)	3243 (5)	33 (2)
C(34B)	−2224 (6)	1467 (6)	3211 (4)	31 (2)
C(44B)	−1636 (6)	2130 (6)	4054 (4)	25 (2)
C(54B)	−2109 (6)	1436 (6)	4823 (5)	31 (2)
C(64B)	−1669 (7)	2087 (7)	5674 (5)	40 (2)
O(64B)	−1758 (5)	3071 (5)	5747 (4)	76 (11)*
O(45B)	−3518 (4)	−550 (4)	3935 (3)	32 (1)
O(25B)	−4664 (5)	−4169 (5)	2689 (4)	56 (11)*
O(35B)	−4632 (5)	−2075 (5)	2505 (3)	84 (11)*
O(55B)	−4667 (4)	−3213 (4)	4888 (4)	37 (1)
C(15B)	−4532 (7)	−3845 (7)	4217 (5)	36 (2)
C(25B)	−4885 (7)	−3572 (6)	3357 (5)	34 (2)
C(35B)	−4236 (6)	−2343 (6)	3266 (4)	29 (2)

Table 2 *continued*

	x	*y*	*z*	$U_{(iso/eq)}$
	CD: Molecule B			
C(45B)	−4313 (6)	−1675 (6)	4045 (4)	27 (2)
C(55B)	−3997 (6)	−2050 (6)	4856 (5)	31 (2)
C(65B)	−4121 (7)	−1505 (7)	5672 (5)	43 (2)
O(65B)	−5224 (5)	−1691 (5)	5741 (3)	102 (11)*
O(46B)	−3421 (4)	−3578 (4)	4202 (3)	33 (1)
O(26B)	−1328 (5)	−5332 (5)	3347 (4)	70 (12)*
O(36B)	−3277 (8)	−5120 (8)	2982 (6)	114 (23)*
O(56B)	−1895 (5)	−4618 (5)	5455 (3)	43 (1)
C(16B)	−1240 (7)	−4660 (7)	4795 (5)	38 (2)
C(26B)	−1986 (7)	−5210 (7)	3996 (5)	43 (2)
C(36B)	−2507 (8)	−4543 (8)	3717 (6)	51 (2)
C(46B)	−3140 (7)	−4390 (7)	4429 (5)	37 (2)
C(56B)	−2438 (7)	−3978 (7)	5287 (5)	38 (2)
C(66B)	−3150 (8)	−4122 (8)	6033 (6)	51 (2)
O(66B)	−4008 (6)	−5252 (6)	6008 (5)	169 (15)*
	Solvent molecules			
	x	*y*	*z*	$U_{(iso/eq)}$
O(W1)	3263 (8)	6557 (8)	8052 (6)	96 (3)
O(W2)	3044 (7)	6397 (7)	6276 (5)	87 (2)
O(W3)	6640 (6)	3094 (6)	8060 (5)	69 (2)
O(W4)	6293 (6)	2961 (6)	6265 (5)	70 (2)
O(W5)	9760 (5)	4421 (5)	7084 (4)	47 (1)
O(W6)	4509 (5)	4414 (5)	7195 (4)	51 (2)
O(W7)	4678 (5)	9516 (5)	7207 (4)	51 (2)
O(W8)	3069 (8)	6681 (8)	2292 (6)	94 (3)
O(W9)	7414 (8)	3783 (8)	1831 (6)	98 (3)
	Guest molecules			
	X	*Y*	*Z*	$U_{(iso/eq)}$
O(1)	568 (17)	623 (18)	−257 (12)	94 (4)
C(11)	916 (17)	979 (18)	1135 (12)	94 (4)
C(21)	289 (17)	402 (18)	416 (12)	94 (4)
C(31)	−721 (17)	−509 (18)	353 (12)	94 (4)
O(2)	−84 (47)	−1533 (48)	2730 (34)	131 (13)
C(12)	−480 (47)	−753 (48)	3817 (34)	131 (13)
C(22)	−591 (47)	−1016 (48)	3102 (34)	131 (13)
C(32)	−1274 (47)	−710 (48)	2725 (34)	131 (13)
O(3)	−1032 (46)	−1001 (46)	6612 (35)	136 (13)
C(13)	282 (46)	733 (46)	6895 (35)	136 (13)
C(23)	−295 (46)	−349 (46)	7047 (35)	136 (13)
C(33)	−117 (46)	−849 (46)	7696 (35)	136 (13)
O(4)	450 (42)	107 (42)	7633 (32)	123 (11)
C(14)	−859 (42)	−1527 (42)	7078 (32)	123 (11)
C(24)	−230 (42)	−411 (42)	7105 (32)	123 (11)
C(34)	−262 (42)	271 (42)	6542 (32)	123 (11)

(*) $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

Starred *u* parameters were refined anisotropically.

Macrocyclic ring conformation

Both crystallographically independent α-CD molecules (A and B) of the complex occur in a conformation which may be considered as 'relaxed' as it is typically found in all channel types complexes. The two α-CD molecules of a dimer are shifted laterally to each other by 1.5 Å. The average bond distances and angles are in the correct range for the twelve independent glucose residues but slight differences exist between the two α-CD hexagons of the dimer.

The O(4) planes of the α-CD molecules are almost parallel (4°), inclined at 8° and 9°, respectively, to the **ab** plane. The distances (Å) to the least-squares plane, given in Table 3, vary between −0.09 and 0.08 for O(4A) plane, and −0.10 and 0.08 for O(4B). The distances O(4n)-O(4n+1) are given in Fig 3. In molecule A, slight elliptical distortions occur in the geometry of the hexagon; the difference in the longest and the shortest diagonal distances is 0.45 Å in contrast to the value of 0.16 Å observed in molecule B. The tilt angles range from 7.9° to 20.7° in molecule A and between 7.3° to 13.1° in molecule B. Such distortions occurring in the two α-CD molecules of the dimer have been observed in all structures of this kind of packing. However it appears that the acetone molecule seems to fit better in the less geometrically regular α-CD molecule as is evidenced by the presence of an undisordered partially occupied site located deeper in the α-CD cavity of molecule A. The torsion angles

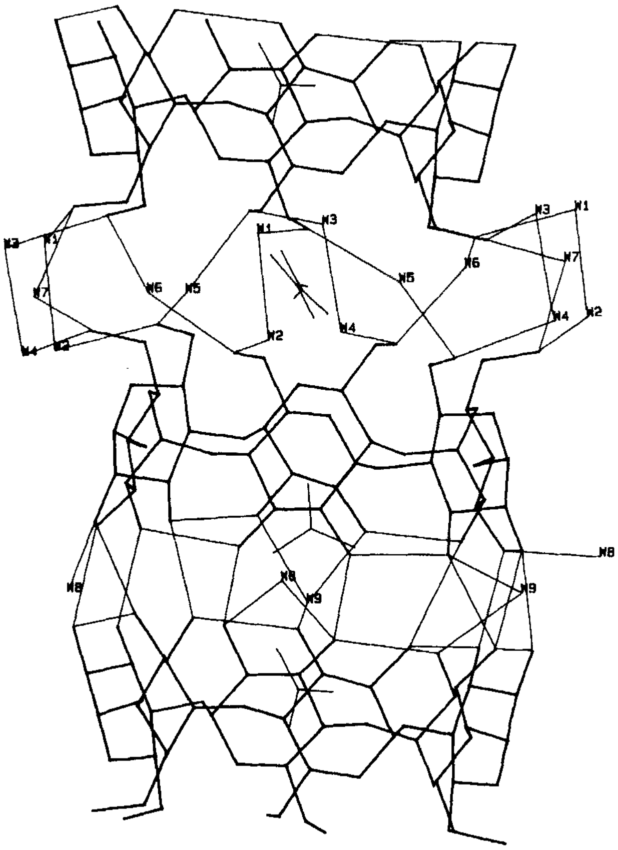


Figure 1 Head-to-head stacking of the α-CD dimers showing the secondary (red) and the primary (yellow) hydroxyl hydrogen bonding network. (See Colour Plate I at the back of this issue.)

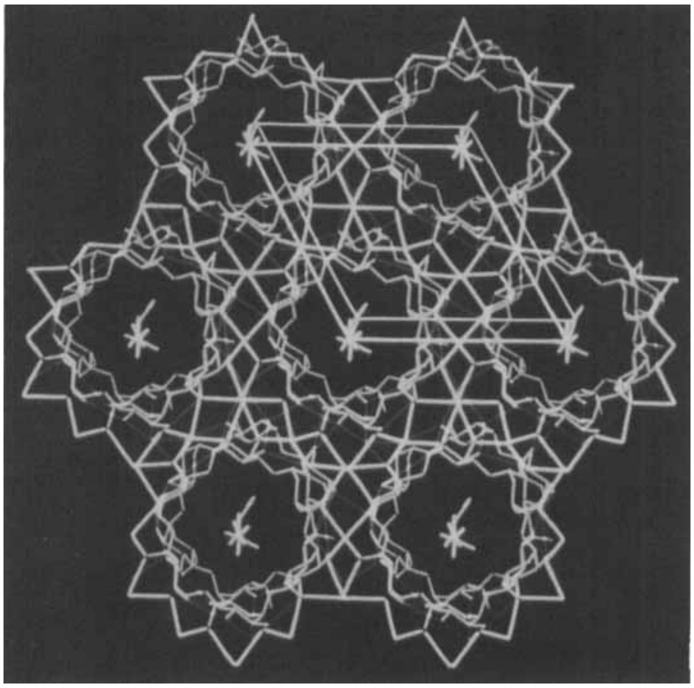


Figure 2 Hexagonal stacking of the α-CD molecules viewed along the **c** axis showing the secondary (red) and the primary (yellow) hydroxyl hydrogen bonding network. (See Colour Plate II at the back of this issue.)

concerning the orientation of the C(6)-O(6) bonds occur in the range 50.0–65.6°, and, 49.9–62.0°, respectively, for A and B, showing the gauche–gauche conformation for all the residues. This implies that all the C6-O6 bonds point away from the centers of the α-CD molecules. The O(2)-O(3) distances between the neighbouring glucose units reveal the probable existence of intramolecular hydrogen bonds.

The residues of molecule A are numerated 1 through 6 in a clockwise direction and those of molecule B in a counterclockwise. 3B and 6B represent the residues vertically above, respectively, 6A and 3A. The best approximate two-fold axis of the dimer is nearly perpendicular to the **a**-axis since there exists a close correlation as well between tilt angles as between torsion angles of the pseudo-related residues (1A-4B, ...).

Hydrogen bonding

Strong intermolecular hydrogen bonding is realised either between hydroxyl groups themselves or between water molecules and hydroxyl groups. No disorder was found, neither in the water nor in the primary hydroxyl positions. All water molecules are located outside of the dimer cavity.

There exists no direct intermolecular primary hydroxyl hydrogen bonding. However, the role played by the primary hydroxyl groups in the cohesion of the structure is essential. They ensure the cohesion in the **ab**-plane as well as along the **c**-axis by fixing a very regular pattern of seven water molecules occurring either as doublets, OW(1)-OW(2) and OW(3)-OW(4), or singlets OW(5), OW(6) and OW(7).

The seven water molecules are situated at levels located between the primary hydroxyl faces O(6A) and O(6B) which are nearly parallel (1.4°). As is shown in Fig 4, each of the twelve independent primary hydroxyl groups is twice hydrogen bonded to water molecules, alternately to one singlet molecule and to one molecule of a doublet. The strong bonding between the channels of dimers in the **ab** plane arises from the particular positions of the seven water molecules (Fig 5). The two doublets are almost in pseudo-ternary axial position, with respect to an α-CD dimer centered at $x=0$, $y=0$, such that they are arranged with their two translation equivalent ones in a pseudo-hexagonal pattern ensuring the cohesion between one α-CD dimer and its six surrounding ones. The three singlets are almost in pseudo-binary axial symmetry positions leading also to a pseudo-hexagonal pattern with their translation equivalent ones, ensuring again the cohesion between one α-CD dimer and its six neighbours.

The O(2)-O(3) faces are linked by direct hydrogen bonds O(2nA)... O(3mB) and O(2mB)-O(3nA) between face-to-face glucose units following a scheme showing significant distortions with respect to those previously reported (Fig 4). These others[4–7] were very regular since almost all such possible direct hydrogen bonds were present and reinforced by some O(3nA)... O(3mB)

Table 3 Geometrical data for A and B α-CD molecules

	Cyclodextrin A	*Cyclodextrin B*
O41	0.08	0.08
O42	−0.06	−0.10
O43	0.05	0.06
O44	−0.06	−0.01
O45	0.08	0.00
O46	−0.09	−0.03

O4 Heights from O4 planes (Å)

	Cyclodextrin A	*Cyclodextrin B*
O41–O44	8.774 (4)	8.485 (9)
O42–O45	8.429 (10)	8.543 (9)
O43–O46	8.326 (9)	8.386 (6)

O4–O4 Diagonal distances (Å)

	Cyclodextrin A	*Cyclodextrin B*
Glucose 1	20.7 (2)	10.0 (6)
Glucose 2	7.9 (4)	12.9 (5)
Glucose 3	11.5 (3)	7.3 (3)
Glucose 4	9.7 (6)	13.1 (2)
Glucose 5	13.5 (5)	8.7 (3)
Glucose 6	13.6 (3)	10.5 (4)

Tilt Angles (°)

	Cyclodextrin A	*Cyclodextrin B*
Glucose 1	50 (1)	62 (1)
Glucose 2	56 (1)	59 (1)
Glucose 3	56 (1)	50 (1)
Glucose 4	66 (1)	51 (1)
Glucose 5	57 (1)	58 (1)
Glucose 6	50 (1)	54 (1)

Torsion Angles C4-C5-C6-O6 (°)

short contacts. Here, direct bonds are absent in two adjacent face-to-face units (3A,6B and 4A,5B) but there exist two O(2nA)... O(2m + 1B) short contacts between glucose units (3A-5B and 4A-4B) reinforced by three others: two O(3nA)... O(3mB), 4A-5B and 5A-4B, and one O(3nA)... O(3m − 1B), 2A-2B. There are also short contacts between secondary hydroxyls of adjacent dimers reinforcing the cohesion between the channels, Table 4.

The water molecule O(W8) is situated almost in a pseudo-ternary axial position at O(2)-O(3) face level and it is engaged, as well as its two translation equivalent ones, in hydrogen bonds with three secondary hydroxyl groups (two with molecule A and one with molecule B) contributing to the cohesion between the channels. The role of the last water molecule OW(9) deserves comment as it contributes to reinforcing the cohesion between the O(2)-O(3) faces by linking secondary hydroxyls which are not directly hydrogen bonded.

The acetone chain

In the last step of the refinement, one non-disordered partially occupied site (site 1) of the acetone molecule was clearly located within the cavity of the α-CD molecule A. However residual electron density peaks (about 1 eÅ^{-3}), not directly interpretable, were distinguished within the cavity of the dimer. A detailed analysis of the difference Fourier maps by means of molecular graphics led us to suggest three other partially occupied sites for the acetone molecule.

Table 4 Interdimer secondary hydroxyl short contacts

	Distance (Å)	*Translation*
O21A-O24B	2.88	$x+1,y,z$
O31A-O23A	2.85	$x+1,y+1,z$
O31A-O36B	3.04	$x+1,y+1,z$
O26A-O25B	2.79	$x+1,y+1,z$

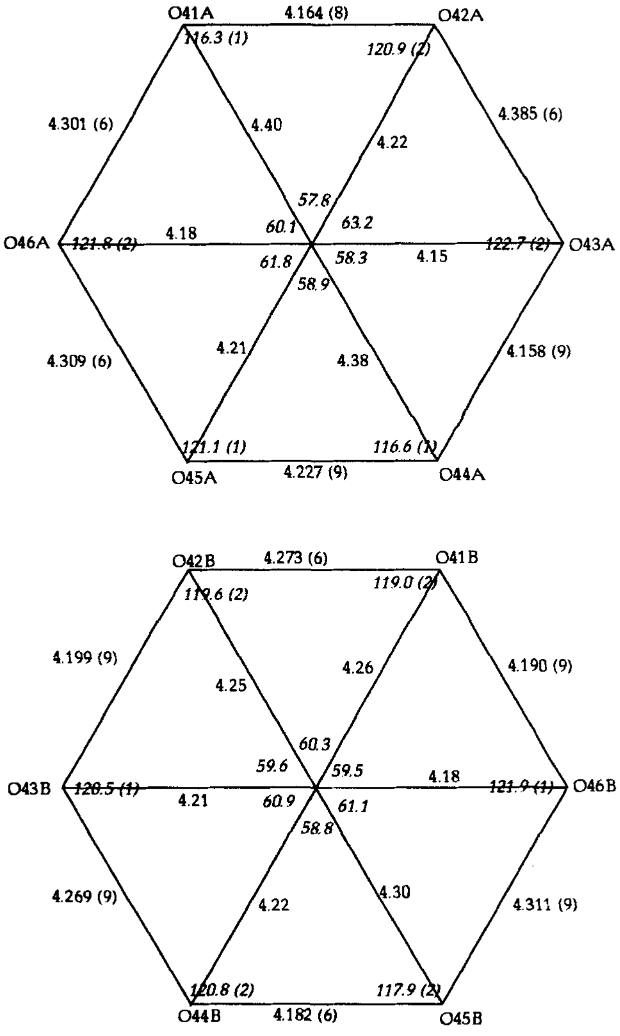


Figure 3 Bond distances and angles of the O4 hexagon for A and B molecules.

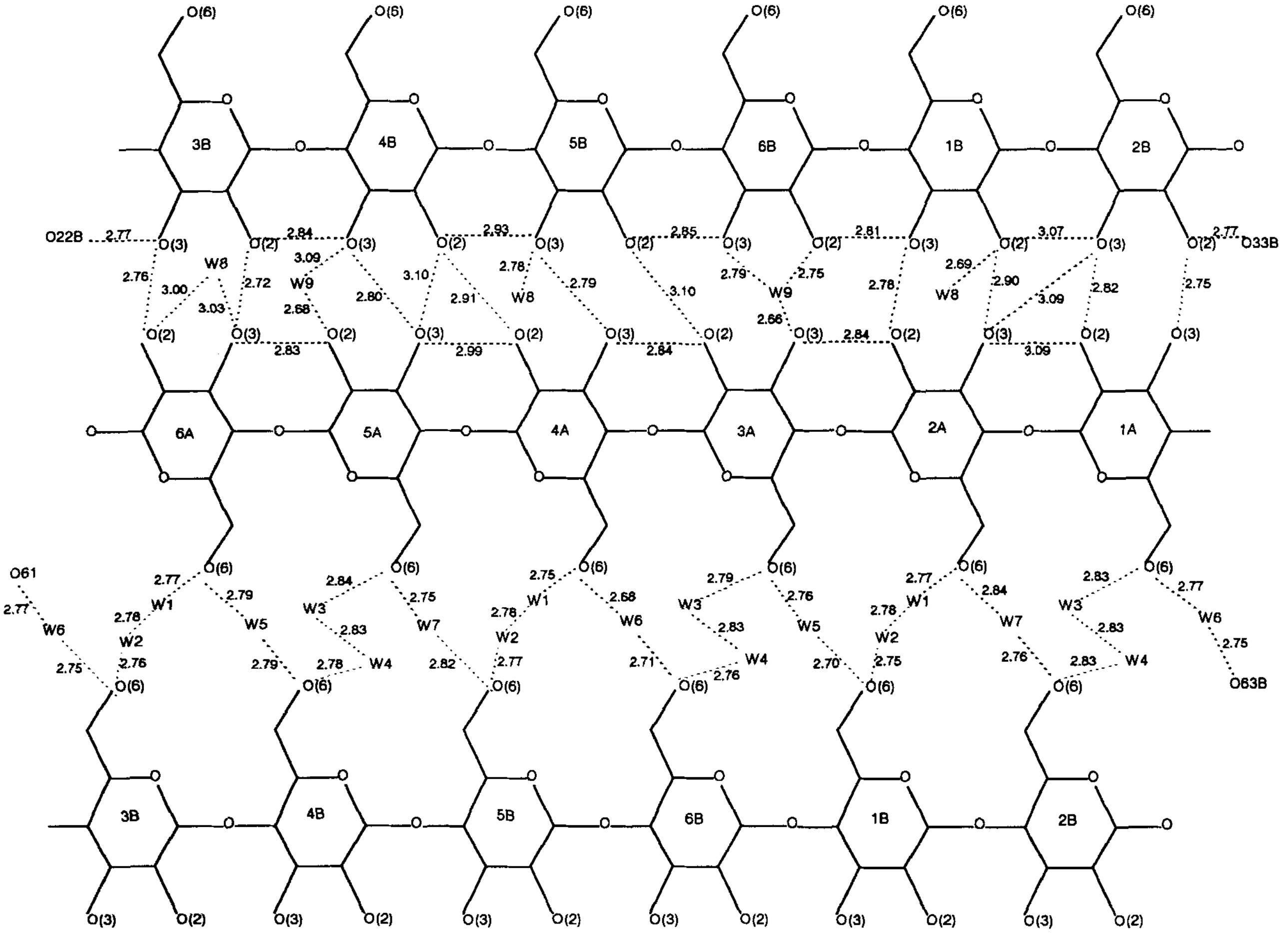


Figure 4 Probable schemes for hydrogen bonding.

A difference Fourier map calculated without any contribution from acetone molecule ($R = 0.079$), represented in Fig 6, revealed clearly the position of the site 1, an occupancy factor of 0.4 being determined approximately from the height of the electron density. This confirmed the results obtained during the refinement. Moreover, it was evident that two flattened electron density areas exist within the cavity of the dimer, realising an infinite chain in the interior of the dimeric cavity. It appeared clearly that acetone molecule could fit in these areas.

Taking into account the contribution of the acetone in site 1, ($R = 0.073$) further difference Fourier maps led us to determine two other sites in the same area located between the O6 faces of the two independent α-CD molecules (sites 2 and 3), and then, another site (site 4) located in the cavity of the α-CD molecule B. The occupancy of each of these three sites is estimated at 0.20. Thus, the approximate guest occupancy sums to 1. Although the R factor ($R = 0.069$) does not differ significantly after introducing the contribution of the acetone in the three new sites, the difference Fourier map was cleared up. There was no residual electron density peak higher than 0.5 eÅ^{-3}, except one near a water molecule (0.6 eÅ^{-3}). In all these calculations the largest negative peak was (−0.3 eÅ^{-3}).

In site 1, the acetone molecule is clearly located deeper in the cavity of the α-CD molecule than in site 4. It is CH... O hydrogen bonded to two diametrically opposite O4 atoms: O41A and O44A, respectively, 3.48 and 3.54 Å. These atoms correspond to the longest diagonal distance of the O4 hexagon. This is the sole short contact involving acetone.

In terms of stoichiometry the complex corresponds to 2 α-CD molecules per acetone as would be measured by such techniques as elemental analysis, NMR, or thermogravimetric analysis. It is evident that if models of the compound has been built solely on the basis of such measurements the proposed structures would have differed from that which we have observed. What is seen, is that the acetone may occupy several distinct, not fully occupied sites.

Measurement of simple stoichiometry has been given considerable emphasis, this study suggests that extreme care must be taken in any form of interpretation of structure based on such types of measurement.

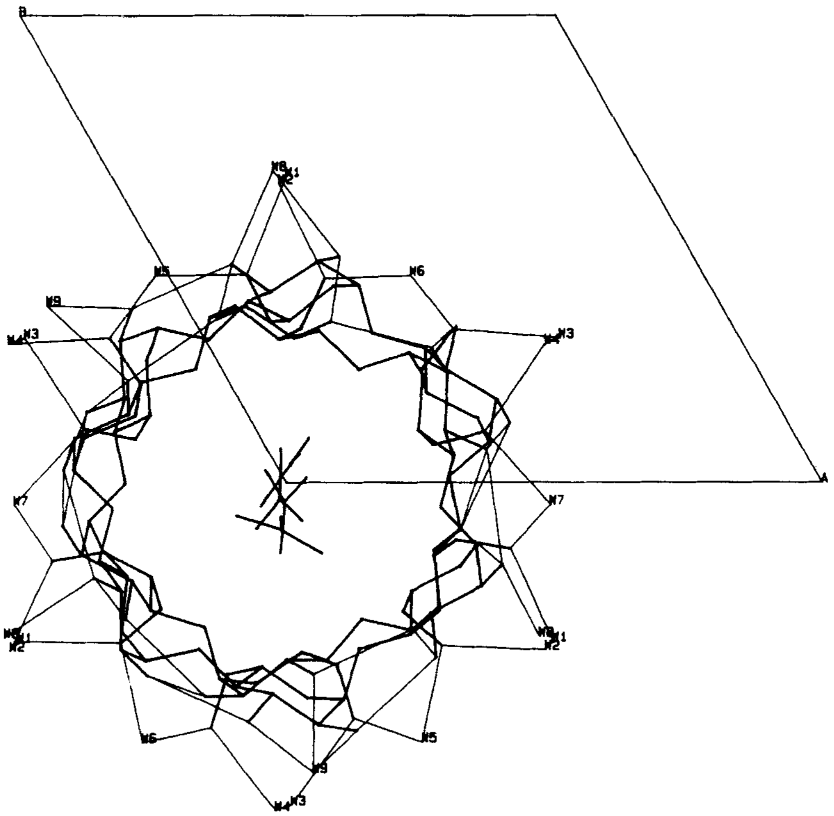
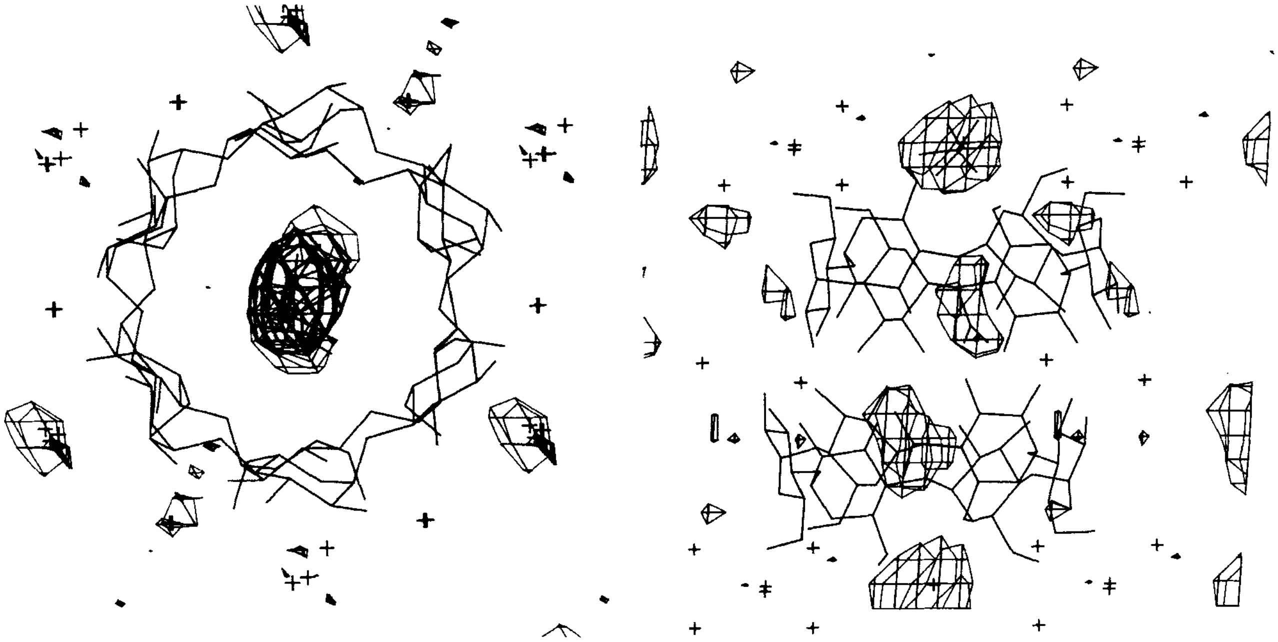


Figure 5 Molecular graphics representation of the possible hydrogen bonding network viewed along the c axis. (See Colour Plate III at the back of this issue.)



(a) (b)

Figure 6 (a) Residual electron density with no acetone molecule contribution contoured at 0.5 eÅ^{-3}, viewed along the c axis; (b) viewed perpendicular to the c axis. (See Colour Plate IV at the back of this issue.)

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