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The crystal structure of the 1:1 inclusion complex of β-cyclodextrin with squaric acid

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Abstract

The crystal and molecular structure of the 1:1 inclusion complex of β-cyclodextrin (cyclomaltoheptaose) with squaric acid (3,4-dihydroxycyclobutene-1,2-dione) was determined by X-ray diffraction. The complex crystallizes in the monoclinic $P2_1$ space group and belongs to the monomeric cage-type, characterized by a herringbone-like packing motif. Co-crystallized water molecules are present on seven sites, of which six are fully occupied. The guest molecule is placed inside the β-cyclodextrin cavity, perpendicular to the plane defined by the glycosidic O-4*n* atoms, and held in place by direct and water-mediated hydrogen bonds mainly involving symmetry-related β-cyclodextrin molecules. The accommodation of the planar guest molecule into the β-cyclodextrin cavity determines a significant distortion of the latter from the sevenfold symmetry. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Crystal structure; β-Cyclodextrin; Squaric acid; Inclusion complex

1. Introduction

Cyclodextrins (CD) are well known for their ability to form inclusion complexes with a variety of molecules, in particular with those having a hydrophobic character.[1,2] Because of this property, CDs have found considerable attention in supramolecular chemistry[3,4] and several practical utilizations, e.g., as solubilizers and carriers in processes of biotechnological[5,6] and pharmaceutical[7–9] interest are well settled.

On the other hand, complexes of CDs with molecules with a pronounced hydrophilic character are less common and more difficult to obtain, especially from aqueous solution, even though some X-ray structures of differently hydrated forms of cyclodextrins have been determined[10–12] and examples of inclusion of polar compounds of low-molecular weight have also been reported.[2,13,14] In this kind of complexation, a difficult point is to ascertain the exact geometry and topology of the complex. A hydrophilic guest should normally prefer a location outside the hydrophobic cavity or, at least, close to the rim of the macrocycle. However, for β-CD, both cage-type and channel-type complexes have been documented with relatively small guests, so the prediction of the solid-state motif of the complex remains elusive.[2,12]

3,4-Dihydroxycyclobutene-1,2-dione (squaric acid, H_2SQ, **1**) belongs to the so-called 'oxo-carbons' class[15] and has some peculiar

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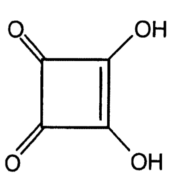
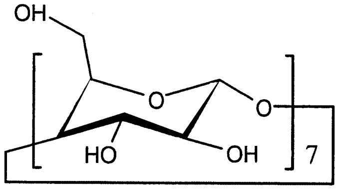
properties. The two enolic hydroxyl groups are rather acidic (pK_a 0.3 and 3.5)[16] and the dianion, SQ^{2-}, is planar, with a fully delocalized electronic structure and is credited with some aromatic character.[17–20] The presence in the same moiety of H-bonding donor and acceptor groups makes this water-soluble molecule, in its various ionization states, a good candidate to play an interesting role in driving the self-assembly of systems based on H-bonding interactions, either in solution or in the solid state.[21,22]

In this work, we describe the crystal and molecular structure of the 1:1 inclusion complex formed between squaric acid, **1**, and β-cyclodextrin, **2**, as determined by X-ray diffraction.



1 H$_2$SQ



2 β-CD

2. Experimental

Crystallization of the complex was achieved by slow evaporation at rt of a 5-mL aq solution containing 0.1 mmol of β-CD and 1.0 mmol of squaric acid. Crystals formed within 2 months, and turned out to be stable in the absence of their mother liquor. A crystal of approximate dimensions 0.20 × 0.15 × 0.10 mm was mounted on a glass fiber and coated with epoxy. Cell parameters were obtained by least-squares refinement of the angular positions of 48 accurately centered reflections with $12 < \theta < 20°$. Intensity data were measured on a Philips PW1100 four circle diffractometer using graphite-monochromated Cu K$_\alpha$ radiation ($\lambda = 1.54178$ Å) in the $\theta - 2\theta$ scan mode up to $\theta = 60°$. Intensities were corrected for Lorentz and polarization effects. No absorption correction was made. Three standard reflections, monitored every 50 reflections, showed a linear intensity decay of 11%. Data were re-scaled accordingly.

The structure was solved by molecular replacement, by application of the PATSEE program,[23] using the coordinates of the β-CD undecahydrate at 42% humidity[11] (deprived of the primary hydroxyl O atoms) as the search fragment. A set of 250 phases, corresponding to the fragment positioning giving the best combined figure of merit, was used as input for the structure expansion with the tangent formula, using the SHELXS-97 program,[24] which allowed the location of 89 atoms, corresponding to the β-CD and squaric acid molecules, and four water molecules. The remaining three water molecules and the minor occupancy sites of the disordered primary hydroxyl groups were located on subsequent difference Fourier maps.

Refinement was carried out by full-matrix block least-squares on F^2, using all data, by application of the SHELXL-97 program,[25] with all non-H atoms anisotropic, and allowing the positional parameters and the anisotropic displacement parameters of the non-H atoms to refine at alternate cycles. Two primary hydroxyl groups of the β-CD molecule, O-61 and O-64, are disordered over two sites, the population parameters of their major sites being 0.65 and 0.70, respectively. Interatomic distances suggested that the occurrence of the O-7W water molecule is compatible only with the major site of the O-61 atom. Therefore, the population parameter of O-7W was set at 0.65. A planarity restraint was applied to the squaric acid molecule. Restraints were also applied to the anisotropic displacement parameters of the atoms of the squaric acid, the co-crystallized water molecules, and the disordered hydroxyl groups. The atoms of the squaric acid display large anisotropic displacement parameters, indicating the possibility of some disorder of the guest molecule within the β-CD cavity. However, despite considerable effort, the data did not allow to model such disorder satisfactorily. H-atoms of the β-CD molecule were calculated at idealized positions. In particular, the position of the H-atom of each hydroxyl group was selected among the three staggered positions as the one forming the best hydrogen bond. H-atoms were refined as riding, with U_{iso} set equal to 1.2 (or 1.5 for the hydroxyl groups) times the

U_{eq} of the parent atom. No attempt was made to assign H atoms either to the squaric acid or to the co-crystallized water molecules.

Crystallographic illustrations were prepared with the program ORTEP-3 for Windows.[26] Geometrical calculations were performed with the program PARST96.[27]

3. Results and discussion

The 1:1 inclusion complex of β-CD with squaric acid, as determined by X-ray diffraction, is illustrated in Fig. 1 with atom numbering. Relevant data describing the molecular geometry and conformation of the β-CD molecule are summarized in Table 2. The glycosidic O-4*n* atoms are only approximately co-planar. The largest displacement from the average plane are observed for the O-45 and O-47 atoms [0.259(5) and −0.346(5) Å, respectively]. The O-4*n*···O-4(*n* + 1) distances vary between 4.209(7) and 4.491(8) Å. The values of the O-4(*n*-1)···O-4*n*···O-4(*n* + 1) angles, varying from 122.7 to 133.6°, are within ± 6° from the 128.6° value of the regular heptagon. The glucose units have the usual $^4C_1$ chair conformation, with the Q_T and θ_2 puckering parameters[28] ranging from 0.521(7) to 0.580(7) Å and from 172.5(9) to 177.9(8)°, respectively. The tilt angles of the glycopyranose residues, defined as the angle between normals to the average plane encompassing the O-4*n* atoms and to the individual planes defined by the O-4(*n*-1), C-1*n*, C-4*n*, and O-4*n* atoms, range between 3.6(3) and 26.5(3)°. Overall, the geometrical parameters reported above indicate a larger deviation of the β-CD molecule from the sevenfold symmetry in this complex compared to its 'empty', hydrated form.[10,12] Most of the primary hydroxyl groups point outwards from the β-CD cavity, as shown by the gauche$^-$ disposition of the O-5*n*–C-5*n*–C-6*n*–O-6*n* torsion angles. Exceptions are both conformers of O-61 and the major conformer of O-64 that point inwards (gauche$^+$ orientation). The macrocycle is stabilized by the usual ring of O-3*n*···O-2(*n* + 1) intramolecular hydrogen bonds, the geometrical parameters of which are reported in Table 2.

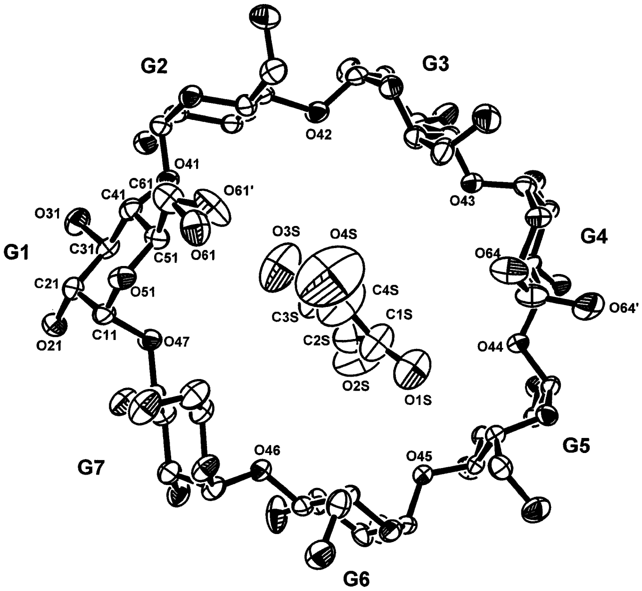


Fig. 1. ORTEP[26] view of the β-CD–squaric acid complex with numbering scheme of the host and guest molecules. C-*mn* and O-*mn* denote the *m*th atom within the *n*th glucosidic residue. The minor occupancy sites of primary hydroxyl O atoms of residues 1 and 4 are labelled as O-61′ and O-64′, respectively. C*i*S and O*i*S refer to the squaric acid atoms. Hydrogen atoms and co-crystallized water molecules are omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

The squaric acid molecule is placed inside the β-CD cavity, perpendicular to the plane defined by the O-4*n* atoms, the angle between normals to the squaric acid and the O-4*n* atoms planes being 90.1(2)°. The line passing through midpoints of the C-1S–C-4S and C-2S–C-3S bonds forms an angle of 12.5(4)° with the normal to the O-4*n* atoms plane. The O-1S and O-4S atoms approach the rim formed by the C-6*n* atoms, while the remaining atoms of the guest molecule are more deeply embedded into the β-CD cavity.

The values of the C-1S–C-4S and C-3S–C-4S bond distances of the squaric acid molecule are 1.393(19) and 1.410(19) Å, while the C-1S–C-2S and C-2S–C-3S bonds are slightly longer [1.457(18) and 1.460(17) Å, respectively]. The C-*i*S–O-*i*S bond distances have values of 1.211(14) and 1.182(14) Å at C-1S and C-2S, respectively, while 1.335(15) Å at C-3S and 1.320(18) Å at C-4S. The bond distances reported above are overall closer to the geometry reported for the hydrogen squarate anion[22,29–34] than either the fully protonated squaric acid[35] or the squarate dian-

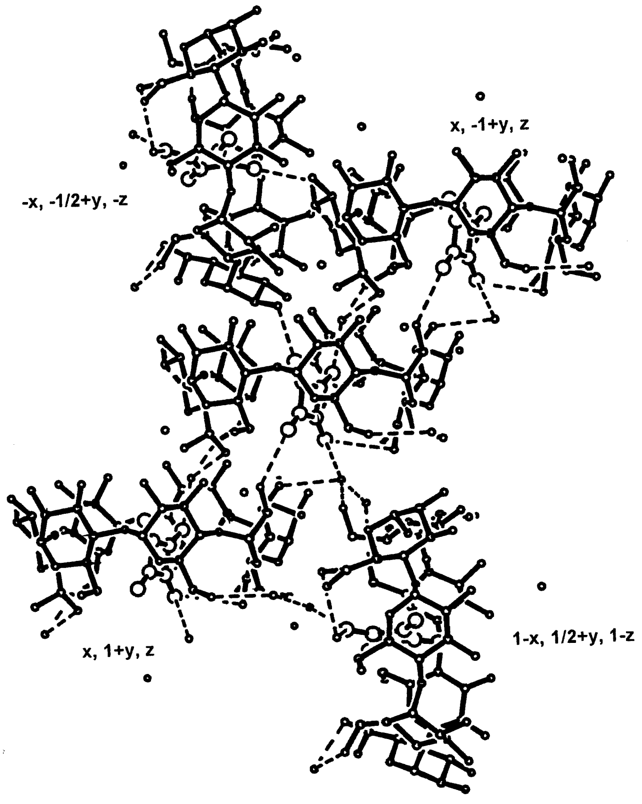


Fig. 2. Packing mode of the β-CD–squaric acid complex. Atoms of the squaric acid molecule are represented as large circles. Symmetry equivalences of the β-CD molecules are indicated. Hydrogen bonds connecting the guest molecule to β-CD molecules, either directly or through water bridges, are shown as dashed lines.

ion.[21,22,36–38] However, care must be taken in attempting to infer the protonation state of squaric acid in the complex from its geometry, since the large displacement parameters associated with the host atoms add uncertainty to their bond distances.

There are no direct hydrogen bonds between β-CD and its guest, although a number of van der Waals contacts within 4.00 Å and four C–H···O interactions are observed between host and guest molecules (Table 3). Intermolecular hydrogen bond parameters are listed in Table 4. Since H-atoms of β-CD were calculated, and those of the co-crystallized water molecules could not be located, the directionality of the hydrogen bonds, as reported in Table 4, is tentative. Only a single, water (O-7W) mediated interaction is observed between O-4S and O-61 (major occupancy site) within the same asymmetric unit. All other hydrogen bonds formed by the squaric acid molecule, either direct or water-mediated, involve symmetry-related β-CD molecules (Fig. 2). More specifically: (i) The O-1S and O-2S atoms are hydrogen bonded with the $(x,\ 1+y,\ z)$ symmetry equivalent of O-27 and with the $(-x,\ -1/2+y,\ -z)$ symmetry equivalent of O-24, respectively. (ii) The O-3W water molecule acts as a bridge connecting the O-3S atom with O-63 and O-64 of the $(x,\ -1+y,\ z)$ equivalent of the β-CD molecule, and with the $(-x,\ -1/2+y,\ -z)$ equivalent of O-34. (iii) The O-4S atom is hydrogen bonded to the O-5W and O-7W

Table 1
Crystal data and structure refinement for the β-CD–squaric acid complex

Empirical formula	$C_{42}H_{70}O_{35}\cdot C_4H_2O_4\cdot(H_2O)_{6.65}$
Formula weight	1366.83
Temperature (K)	293(2)
Wavelength (Cu K_α) (Å)	1.54178
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	15.231(3)
b (Å)	10.068(3)
c (Å)	21.117(3)
β (°)	110.16(5)
V (Å^3)	3039.8(12)
Z	2
D_{calcd} (Mg/m^3)	1.493
Absorption coefficient (mm^{-1})	1.189
$F(000)$	1449
Crystal size (mm)	0.20 × 0.15 × 0.10
θ Range for data collection (°)	4.47-60.05
Limiting indices	$-17 \le h \le 16$ $0 \le k \le 11$ $0 \le l \le 23$
Reflections collected/unique/observed $[I \ge 2\sigma(I)]$	4950/4809/3408
R_{int}	0.0465
Completeness to $\theta = 60.05°$ (%)	99.8
Data/restraints/parameters	4809/135/847
Goodness-of-fit on F^2	0.967
Final R indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0694$, $wR_2 = 0.1816$
R indices (all data)	$R_1 = 0.0947$, $wR_2 = 0.1967$
Weighting scheme	$1/[\sigma(F_o^2)+(0.1528P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.1(4)
$(\Delta/\sigma)_{max}$	0.404
Largest difference peak and hole (e/Å^3)	0.630 and −0.319

Table 2
Relevant geometrical parameters for the β-CD molecule

Residue	D (Å)	φ (°)	d (Å)	α (°)	D_3 (Å)	D_3 (Å) [a]	Angle (°) [a]	Torsion angle (°)
					O-3n···O-2 (n+1)	O-3n−H···O-2 (n+1)	O–H···O	O-5n–C-5n–C-6n–O-6n
G1	4.326(7)	122.67(13)	0.203(5)	21.5(3)	2.993(7)	2.18	175	57.8(10) [88.9(15)]
G2	4.491(8)	130.93(12)	0.198(6)	3.6(3)	2.900(9)	2.25	136	−65.4(8)
G3	4.394(7)	130.14(12)	−0.191(5)	18.4(2)	2.946(9)	2.30	137	−67.4(9)
G4	4.289(7)	127.52(11)	−0.127(5)	26.5(3)	2.845(8)	2.03	170	61.6(11) [−67.6(14)]
G5	4.397(7)	123.10(11)	0.259(5)	11.5(2)	2.961(8)	2.19	158	−62.9(8)
G6	4.486(8)	133.64(12)	0.008(5)	8.2(3)	2.790(10)	2.13	137	−64.4(9)
G7	4.209(7)	129.32(11)	−0.346(5)	12.7(3)	2.762(10)	2.00	154	−70.3(10)

[a] Geometrical values reported without e.s.d.s involve H-atoms at calculated positions.

D = distance between atoms O-4n···O-4(n+1); φ = angle between atoms O-4(n-1)···O-4n···O-4(n+1); d = deviation of O-4n atom from the least-squares optimum plane formed by the seven O-4n atoms; α = dihedral angle between normals to the least-squares optimum plane formed by the seven O-4n atoms and the plane defined by the O-4(n-1), C-1n, C-4n, and O-4n atoms. D_3 = O-3n–H···O-2(n+1) intramolecular H bond parameters. The values of torsion angles in square brackets refer to the minor occupancy sites of O-6n atoms.

water molecules. Atom O-5W is further connected to O-37 (symmetry equivalence: x, $1+y$, z), to O-67 (symmetry equivalence: $1-x$, $1/2+y$, $1-z$), and to O-2W which, in turn, is hydrogen bonded with O-21 (symmetry equivalence: $1-x$, $1/2+y$, $1-z$). Atom O-7W, in addition to the interaction with O-61 within the same asymmetric unit described above, is hydrogen bonded with the (x, $1+y$, z) symmetry equivalent of O-21. Additional β-CD–water and water–water interactions are listed in Table 4.

In summary, four symmetry related β-CD molecules participate directly or indirectly to the hydrogen bonding scheme involving the squaric acid molecule. The resulting packing mode is characterized by layers of herringbone-like motifs, similarly to that observed for the ‘empty’, hydrated form of β-CD and for some complexes with small guests.[2,10,12]

Finally, we have to stress here the following points: (i) The squaric acid moiety, although rather hydrophilic, is entirely buried inside the hydrophobic cavity of the cyclodextrin and is oriented perpendicularly to the mid-plane of the macrocycle defined by the glycosidic oxygen atoms (axial mode of insertion), only slightly emerging from the bottom rim; (ii) No direct O–H···O hydrogen bonds occur between the cyclodextrin and its guest within the same asymmetric unit, but only one indirect water-mediated interaction is observed between O-4S and O-61 atoms, beside a number of van der Waals and C–H···O contacts with the cavity; (iii) The guest molecule determines a distortion of the macrocycle comparable to that reported for the β-CD complexes with largely planar guests such as nicotinamide and benzyl alcohol;[39,40] (iv) The guest molecule, along with the co-crystallized water molecules, play an important role in the context of the intermolecular hydrogen bonding network.

Table 3
Distances between host and guest atoms less than 4.00 Å

Atoms	Distance (Å)
C-1S···O-64	3.906(17)
O-1S···O-64	3.538(14)
O-1S···C-64	3.683(14) [a]
O-1S···C-55	3.457(14) [a]
O-1S···C-56	3.747(13) [a]
O-1S···C-65	3.452(15)
O-1S···C-66	3.823(13)
O-2S···O-45	3.557(13)
O-3S···O-41	3.633(15)
O-3S···C-51	3.735(14) [a]
O-3S···O-47	3.931(12)
O-4S···O-61	3.767(24)
O-4S···O-61′	3.505(34)

[a] C–H···O contacts.

Table 4
Intermolecular hydrogen bonds

Donor	Acceptor	Symmetry equivalence of A	Distance (Å) [a]		Angle (°) [a]
D–H	A		D···A	D–H···A	D–H···A
Between squaric acid and β-CD or water molecules					
O-27–H-27A	O-1S	$x, -1+y, z$	3.031(12)	2.23	168
O-24–H24A	O-2S	$-x, 1/2+y, -z$	2.646(12)	1.83	178
O-3W	O-3S	$x, 1+y, z$	2.531(14)		
O-5W	O-4S	x, y, z	2.827(18)		
O-7W	O-4S	x, y, z	2.485(26)		
Between β-CD molecules					
O-22–H-22A	O-63	$x, -1+y, z$	2.843(10)	2.14	145
O-25–H-25A	O-32	$-x, 1/2+y, -z$	2.776(9)	2.22	125
O-66–H-66	O-62	$1+x, y, z$	2.800(10)	2.19	132
O-64′–H-64′	O-24	$1-x, 1/2+y, -z$	2.932(22)	2.26	145
Between water and β-CD molecules					
O-21–H-21A	O-2W	$1-x, -1/2+y, 1-z$	2.833(10)	2.05	161
O-23–H-23A	O-1W	$-x, 1/2+y, -z$	2.851(7)	2.15	143
O-26–H-26A	O-1W	x, y, z	2.733(9)	1.98	152
O-61–H-61	O-6W	$1-x, -1/2+y, 1-z$	2.974(15)	2.17	167
O-62–H-62	O-6W	$-1+x, y, z$	2.958(18)	2.15	169
O-64–H-64	O-3W	x, y, z	2.837(13)	2.07	157
O-65–H-65	O-1W	$x, 1+y, z$	3.079(9)	2.27	172
O-67–H-67	O-5W	$1-x, -1/2+y, 1-z$	2.735(13)	1.93	168
O-1W	O-35	$1-x, -1/2+y, -z$	2.850(9)		
O-1W	O-55	$x, -1+y, z$	2.971(9)		
O-2W	O-66	x, y, z	2.718(11)		
O-3W	O-34	$-x, 1/2+y, -z$	2.722(8)		
O-3W	O-63	x, y, z	2.714(11)		
O-4W	O-22	$1+x, y, z$	2.677(11)		
O-4W	O-65	$x, -1+y, z$	2.766(11)		
O-5W	O-37	$x, 1+y, z$	2.966(12)		
O-6W	O-67	$1-x, 1/2+y, 1-z$	2.778(16)		
O-7W	O-21	$x, 1+y, z$	2.791(17)		
Between water molecules					
O-2W	O-5W	$1-x, -1/2+y, 1-z$	2.918(15)		
O-6W	O-4W	$x, 1+y, z$	2.783(15)		

[a] Geometrical values reported without e.s.d.s' involve H-atoms at calculated positions.

The resulting packing motif is of the cage type.

4. Supplementary material

Relevant crystal data are reported in Table 1. Full crystallographic details, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 160149. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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