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A supramolecular inclusion complex (1) was prepared between β-cyclodextrin and 8-nitro-quinoline, and its bound structure was investigated by X-ray crystallography in the solid state. The crystallographic study has shown that the inclusion complex 1 belongs to the Monoclinic system (space group: C2) with unit cell dimensions $a = 19.269(5)$, $b = 24.395(7)$, $c = 16.095(4)$Å, $\beta = 107.816(5)^\circ$, and forms a channel-type polymeric supramolecule. In the crystal structure, the β-cyclodextrins exist as a head-to-head dimer by means of extensive hydrogen bonding across the secondary hydrogen groups of two symmetry-dependent β-cyclodextrins. Two guest molecules are included in the cavity of the different β-cyclodextrins, respectively, and the third is sandwiched in the interface of the dimer. The results indicate that the different inclusion behavior of 8-nitro-quinoline in β-cyclodextrin cavity results from differing host-guest hydrogen bonding as well as spatial constraints.

Keywords: Inclusion complex; Crystal structure; Cyclodextrin; Supramolecule

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligomers of 1,4-linked, α-D-glucose monomers that have become the focus of intense study by scientists and technologists interested in application of guest-host complexation, depending on the fact that they act as host molecules to form inclusion complexes with a wide variety of guests [1–4]. This feature is used as ideal prototypes for examining intermolecular interactions associated with molecular recognition and assembly [5–7]. It has been recognized that the binding forces involved in inclusion complexation are host-guest interactions in CD complexes including hydrophobic and van der Waals interaction, and hydrogen bonding, some or all of which may contribute to the formation of a supramolecular system, resulting from the chemical nature of CD and the guest molecule. Therefore, it is important to study these weak interactions, to further our understanding of the nature of the formation of supramolecules and to predict new approaches in drug delivery, enzyme mimics, material science and other frontiers of chemistry [8–10]. On the other hand, the orientation of the organic guest molecule within the CD host is a crucial element of this host–guest interaction and dictates critical properties such as stability of the complex and the catalytic activity of the guest. On this basis, a lot of CD inclusion complexes have been extensively investigated by using a variety of methods such as mass spectrometry, UV/visible spectrometry, and microcalorimetry. However, crystallographic studies provide direct access to this type of structural information [11–22]. These x-ray studies, directed toward an understanding of the conformation and weak interaction involved in the CD complexes, can provide valuable information of the unique nonbonding interactions to obtain more selective functional supramolecular systems. To get insight into the conformation and mechanism of the noncovalent interactions of inclusion complexes at the molecular level, which allow further understanding of molecular recognition and assembly behavior in supramolecular chemistry, in the present study, we prepared a channel-type supramolecular aggregation by the inclusion complex of β-CD with 8-nitro-quinoline, and investigated its binding behavior in the solid state by means of X-ray crystallography, the modes of inclusion are discussed in detail.

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EXPERIMENTAL

Reagents

β-CD of reagent grade was recrystallized twice from water and dried *in vacuo* at 95°C for 24 h prior to use. 8-Nitro-quinoline was commercially available and used without further purification.

Apparatus

The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator at T = 293(2) K. The structures were solved by using direct methods and refined, employing full-matrix least squares on F^2 (Siemens, SHELXTL, version 5.04). Elemental analyses were performed on a Perkin-Elmer 2400C instrument. ^{1}H NMR spectra were recorded in D_2O on a Varian Mercury VX300 spectrometer.

Synthesis of Complex 1

The ethanol solution of 8-nitro-quinoline (1 mmol, 15 ml) was added dropwise to an aqueous solution of β-CD (1 mmol, 25 ml) and stirred at 75°C for 5 h. Then the solution was slowly cooled to room temperature, and was refrigerated for a week, and the precipitate formed was filtered to obtain a white powder. The crude product was dissolved in hot water to make a saturated solution, then the resultant solution was kept at a temperature of ~70°C and was slowly evaporated for 5 days. The crystal formed was collected along with its mother liquor for the X-ray crystallographic analyses. Data for **1**: yield 45%. ^{1}H NMR (300 MHz, D_2O, ppm): δ = 3.40 ~ 3.83 (m, 42H), 4.71 ~ 4.92 (m, 7H), 7.57 ~ 7.64 (m, 2H), 8.14 ~ 8.18 (m, 1H), 8.40 ~ 8.42 (d, 2H), 8.82 ~ 8.83 (d, 1H). Anal. Calcd. for $C_{55.5}H_{79}N_3O_{38}\cdot 11H_2O$ (1594): C 41.78, H 6.34; N 2.63%; Found: C 41.96; H 5.97; N 2.34%.

X-ray Diffraction Analysis

A single crystal of the inclusion complex **1** suitable for X-ray analysis was glued to a glass fiber and collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum target X-ray tube (Mo Kα radiation $\lambda = 0.71073$ Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator. Data were collected to $2\theta_{max} = 50.00°$. The instrument was equipped with a graphite monochromator. Intensities were collected at room temperature. During data collection, no intensity decay was observed. Corrections for Lorenz and polarization effects were applied. Relevant data collection and structure refinement parameters are summarized in Table I. The most common programs for small molecules and for macromolecules employing direct methods were not able to solve the phase problem. The structure was eventually solved employing SHELXD [23]. Atom co-ordinates and anisotropic thermal parameters were refined for all non-hydrogen atoms using conjugate gradient least-squares in the initial stages, and finally full-matrix least squares on F^2 with the Shelxl97 program [24]. All hydrogen atoms were introduced in idealized positions, those belonging to waters were not introduced. The disordered guest molecule atoms were fixed in a quinoline ring and the bond lengths of C–N and N–O were fixed in 1.45 Å and 1.2 Å, respectively.

TABLE I The crystal data, experimental and refinement parameters of **1**

	Crystal **1**
Molecular formula	$C_{55.5}H_{105}N_3O_{51}$
M_r (g mol^{-1})	1630.43
Crystal system	Monoclinic
Space group	*C2*
Z	4
a (Å)	19.222(7)
b (Å)	24.565(9)
c (Å)	16.002(6)
β (°)	108.530(7)
V(Å^3)	7164(4)
ρ_{calcd} (g cm^{-3})	1.512
F (000)	3468
T (K)	293(2)
Crystal size (mm)	0.32 × 0.28 × 0.24
Range scanned θ (°)	1.39 - 25.00
Index range	−13 < = h < = 22, −28 < = k < = 29, −19 < = l < = 14
Data / restraints / parameters	12407 / 121 / 868
Final R indices [I > 2sigma(I)]	0.1222
R indices (all data)	R1 = 0.1797, wR2 = 0.3565

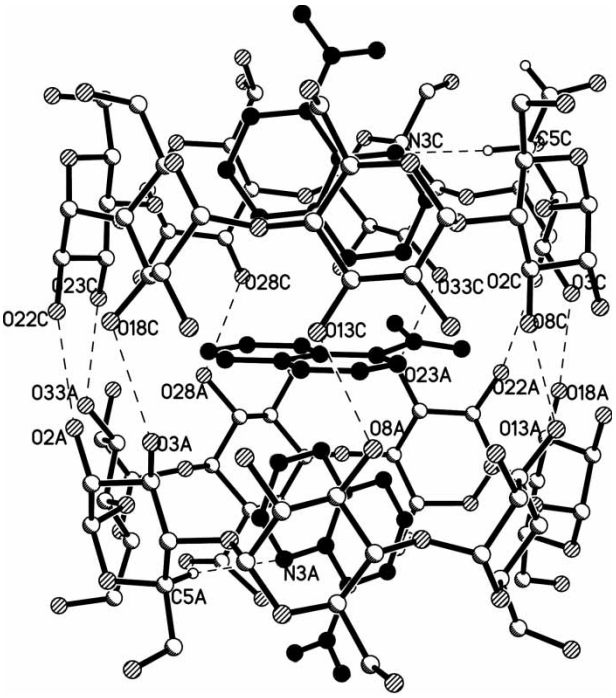

FIGURE 1 View of the inclusion complex of 8-nitro-quinoline and β-cyclodextrin. The hydrogen bonds are indicated by dash lines (the disordered components of the structure are omitted for the purposes of clarity).

RESULTS AND DISCUSSION

Crystal Data of 1

The crystallographic data of **1**[†] was collected from a well-formed, prismatic crystal (0.32 × 0.28 × 0.24 mm) sealed in a glass capillary to prevent loss of the water of crystallization. The crystal data, and the experimental and refinement parameters of 1 are shown in Table I.

Crystal Structure and Molecular Conformations

It is well known that the crystal packing is classified according to three categories: cage-type, channel-type, and layer-type [11]. The inclusion complex **1** belongs to the channel-type, the crystal structure revealed the 2:3 stoichiometry of host and guest molecules. The symmetric unit consists of head-to-head hydrogen-bonded β-CD dimer hosts, 2.5 guest molecules, and several waters of hydration. As shown in Fig. 1, two 8-nitro-quinoline molecules locate in the cavity of the different β-CD molecules, respectively, the third lies flat between two β-CD molecules that form the head-to-head dimer by means of extensive hydrogen bonding across the secondary hydrogen groups of two symmetry-dependent β-CDs (Table II).

TABLE II Bond lengths for hydrogen-bonding interaction observed in the dimer

Interaction [a]	distance (Å)
O33 B ···O23 A	2.7829(8)
O28 B ···O28 A	2.831(12)
O23 B ···O33 A	2.782(8)
O22 B ···O2 A	2.902(9)
O18 B ···O3 A	2.904(10)
O13 B ···O8 A	2.860(9)
O8 B ···O13 A	2.860(9)
O3 B ···O18 A	2.904(10)
O2 B ···O22 A	2.902(9)

[a] A and B denote the CD monomer in the dimer.

In the crystal structure, every β-CD has an approximate 7-fold axis and maintains the round shape of the macrocycle. The parameters describing the macrocyclic conformation of **1** are characterized in Table III. Every glucose residue of β-CD has a $^4C_1$ chair conformation, and seven glycosidic oxygen atoms are coplanar within 0.0067 Å, the dihedral angel of the O-4 plane of the adjacent β-CDs is 1.2°, which indicates that the adjacent β-CDs are almost parallel. However, the deformation of the macrocycle if compared with the conformation typical of uncomplexed β-CD, can be described through the heptagonal rings defined by the O4 atoms bridging the seven glucopyranose units (average values for uncomplexed β-CD: radius of the O4 heptagon = 5.04 Å, values ranging between 4.86 and 5.18 Å, O4(n)···O4(n − 1) distances = 4.31 Å, values ranging between 4.20 and 4.50 Å) [25]. The guest molecule, located in the cavity of β-CD, interacts with the macrocylic host and this causes the deformation in the β-CD ring: (radius of the O4 heptagon = 5.05 Å, values ranging between 4.95 and 5.17 Å, O4(n)···O4(n − 1) distances = 4.38 Å, values ranging between 4.31 and 4.48 Å).

The position of the guest in the β-CD cavity is shown in Fig. 2, one guest molecule is deeply included into a β-CD cavity, with the nitryl group pointing to the primary hydroxyl group. The angle between the molecular axis of the guest and the perpendicular axis to the O-4 plane of β-CD is 0.6°, which show that the guest is almost inserted perpendicularly into β-CD cavity. The ring enters the cavity of the β-CD and makes van der Waals contacts with the atoms constructing the inside wall of the β-CD cavity, while one nitrogen atom, N3, is hydrogen bonded to a methylene group of the same *β*-CD ($d_{[H5A\cdots N3]} = 2.531$ (2)Å, $\Phi_{[C5-H5A\cdots N3]} = 161.4(8)°$). In addition, nitryl oxygen atom, O(38), forms a hydrogen bond with *β*-CD ($d_{[H6AB\cdots O38A]} = 2.545(2)$ Å, $\Phi_{[C6B-H6AB\cdots O38A]} = 145.6(3)°$). As a result, the position of the 8-nitro-quinoline within the *β*-CD cavity is determined by the host-guest interactions

[†]CCDC-261829 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: +44-1223-336-033; or E-mail: deposite@ccdc.cam.ac.uk)

TABLE III Geometrical data describing the β-CD unit of the compounds

	O4(n)-O4(n − 1) (Å)	O4(n)-O4(n+1) − O4(n+2) (°)	C4(n)-O4(n)-C1 (n+1) (°)	Tilt angle [a](°)	Deviation of O-4 atom (Å)[b]
1					
G1	4.410(9)	126.9(2)	119.2(7)	8.1(4)	0.0043
G2	4.325(8)	129.8(2)	118.6(6)	5.7(2)	−0.0002
G3	4.430(8)	130.5(2)	117.4(6)	10.1(2)	0.0009
G4	4.386(8)	125.6(2)	118.8(6)	13.1(2)	−0.0109
G5	4.306(9)	128.8(2)	119.4(6)	9.0(1)	0.0182
G6	4.477(8)	130.7(2)	118.4(10)	11.9(2)	−0.0125
G7	4.321(11)	127.7(2)	117.1(8)	10.9(3)	0.0001

[a] The tilt angle is defined as an angle made by the O(4) plane and the plane through C-1, C-4, O-4, and O-4′. [b] The diviation of each of O-4 atom from the plane through seven O(4) atoms.

which include the van der Waals contacts and hydrogen bond between the host and guest.

On the other hand, the adjacent β-CDs embodied guest molecules form the head-to-head dimer through hydrogen bonds of the secondary hydroxy group. The third guest molecule is sandwiched in the interface of the dimer by means of hydrophobic interaction. Close examination of the 8-nitro-quinoline site shows that the guest lies in the broadest part of the dimer cavity with the positions of the host molecules unperturbed by the presence of the guest. The only interaction between guest and host appears to be the van der Waals contacts between 8-nitro-quinoline H atoms and the hydroxyl groups of β-CD. This indicates that the interface enclosed by a complete network of hydrogen bond also can be considered as a hydrophobic site.

The β-CD dimer further form the channel suprastructure through hydrogen bond interaction. At the same time, the additional water molecules in the hydrophilic interface binding environment participate in interactions (see Fig. 3) with β-CD molecules, typically bridging hydroxyl groups of neighboring β-CD molecules, which contribute to stabilization of the polymeric-like channel supra-structure.

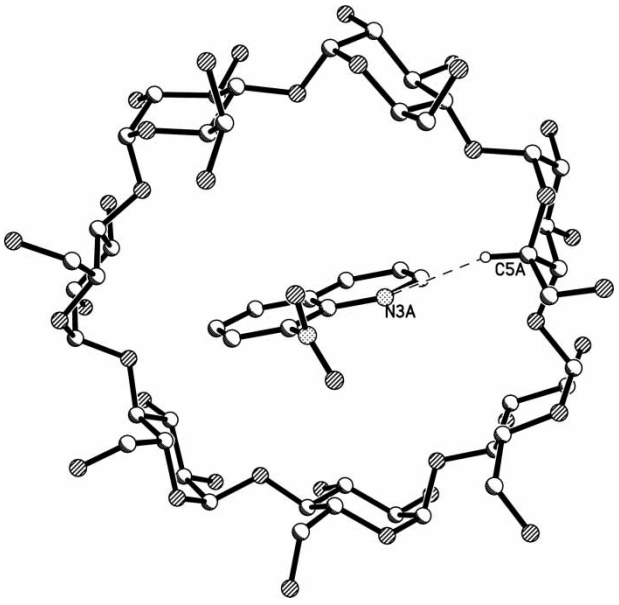

FIGURE 2 View of the inclusion complex of 8-nitro-quinoline and β-cyclodextrin. The hydrogen bonds are indicated by dash lines.

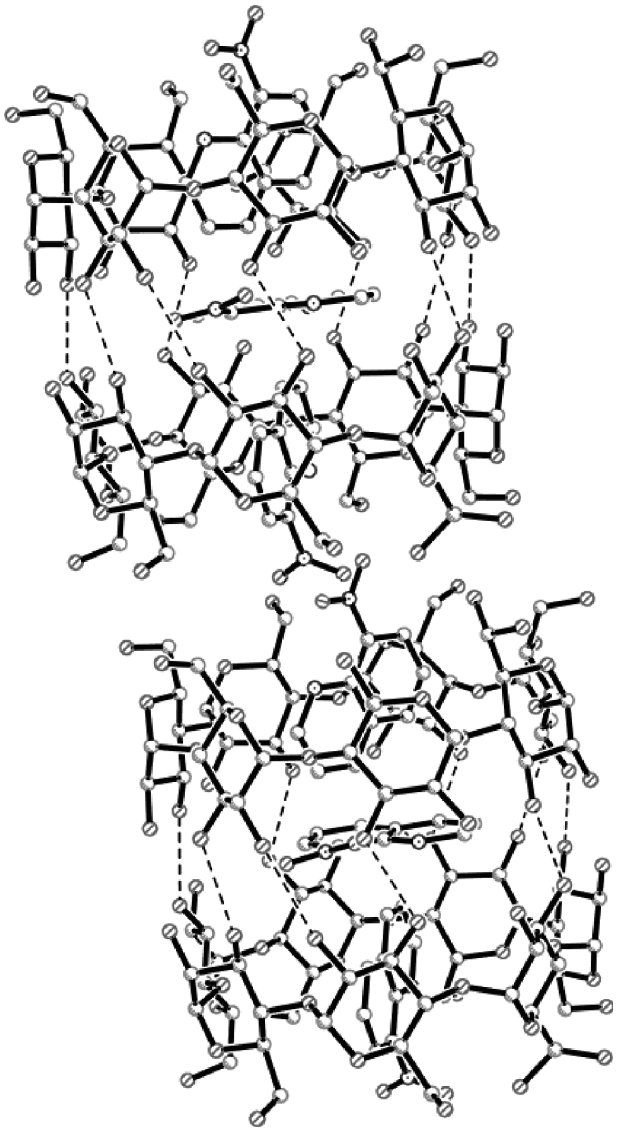

FIGURE 3 The channel structure of the inclusion complex of β-cyclodextrin and 8-nitro-quinoline.

CONCLUSION

A supramolecular inclusion complex was prepared between β-CD and 8-nitro-quinoline, and its binding behavior was investigated by X-ray crystallography in the solid state. The crystallographic study indicates that β-CD and 8-nitro-quinoline form 2:3 inclusion complex in which two guest molecules are embedded in two β-CD cavity respectively and the third lies flat in the space of the interface between β-CDs in the head-to-head dimers. The position of the 8-nitro-quinoline within the β-CD cavity is determined by the host-guest interactions. From the results, it seems that the different inclusion behavior of 8-nitro-quinoline in the β-CD cavity results from differing host-guest hydrogen bonding as well as spatial constrains. Study of the complexation phonomena is useful not only for globally understanding supramolecular aggregation phenomena, but also for designing tailored building blocks for versatile supramolecular aggregates and materials.

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