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Dimeric Complex of Alpha Cyclodextrin with 1,12-Diaminododecane. Comparison with other Alpha Cyclodextrin Dimeric Complexes

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The structure of the complex of alpha cyclodextrin (αCD) with 1,12-diaminododecane has been determined at room temperature. The compound crystallizes in the monoclinic, space group $P2_1$, with $a = 14.10(2)$, $b = 16.91(2)$, $c = 24.45(4)$ Å, $\beta = 97.40(3)^\circ$ and $D_c = 1.398\,\mathrm{gcm}^{-3}$ for $Z = 2$. Refinement based on 5552 observed MoKα reflections with $I > 2\sigma I$ led to a final $R = 0.075$. The diamine molecules thread through two αCD arranged in a head-to-head fashion thus, forming [3]pseudorotaxanes. The amine nitrogen atoms, protruding from the primary hydroxyl sides of the αCD dimer, hydrogen-bond to primary hydroxyl oxygen atoms of consecutive dimers and prevent stacking of the dimers along channels. A comparison of the structure to other dimeric structures of αCD shows differences with respect to geometry and packing of the dimers.

Keywords: Alpha-cyclodextrin, 1,12-diaminododecane, dimer, inclusion complex, [3]pseudorotaxane

INTRODUCTION

This work is part of a systematic investigation of inclusion complexes of α- and β-cyclodextrins with long aliphatic guest molecules [1]. α-Cyclodextrin (αCD) complexes crystallize mainly as monomeric units. With 1,12-diaminododecane, αCD forms a 2:1 complex (ADA), where two αCD macrocucles, arranged head-to-head in almost perfect 6-fold symmetry, enclose one molecyle of the guest. The supermolecule, thus formed, is a [3]pseudorotaxane, since the linear guest threads through two molecules of the host [2]. Dimeric αCD complexes have been observed in the literature with guests such as metallocenes, where a large cavity is required for inclusion [3], or polyiodides with various cations [4], and, surprisingly, acetone [5]. Except for the complex of αCD with cadmium polyiodide [4], the αCD monomers are laterally shifted with respect to each other in all the dimeric structures. The amount of the shifting depends on the guest's dimensions, the bulkier the guest the more distorted the dimer [6]. The present structure comprises an αCD complex where the dimer is undistorted. There is also enough

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evidence that αCD forms dimeric inclusion complexes with other aliphatic molecules of sufficient length such as ω-amino acids and long aliphatic diacids [1C, 7].

RESULTS AND DISCUSSION

Structure of the Inclusion Complex

Crystallographic data is summarized in Table I. The numbering scheme for the host and guest molecules is given in Figure 1; C(A or B) *mn* and O(A or B) *mn* denote the *m*th atom within the *n*th glucosidic residue of the crystallographically independent αCD molecules A and B.

As shown in Table II the αCD molecules possess a near six fold symmetry. The mean value of the angle between the glucosidic oxygen atoms O4*n* is 120(1)°, equal to the angle of the regular hexagon, and the deviations of the O4*n* atoms from their optimum plane are very small. The conformation of each αCD macrocycle is stabilized through intramolecular hydrogen bonds connecting the O3*n* and O2(*n* + 1) atoms of neighboring glucosidic units similar to the βCD dimeric complexes [8]. The O3*n* ... O2(*n* + 1) distances (average 2.88(8) Å, range 2.80 – 3.04 Å) and the angles C3*n* —O3$_n$ ... O2(*n* + 1) (average 114(2), range 108.9 – 118.5°) and O3*n* ... O2(*n* + 1) — C2(*n* + 1) (average 117(4)° range 115.0 – 120.9°) lie within the normal values for H-bonds. In βCD dimers the O3*n* ... O2(*n* + 1) distances are shorter (average value 2.78(2) Å, range 2.74 – 2.82 Å), a fact indicating that in αCD the stabilization is weaker than in βCD.

The αCD dimer is formed *via* OA3*n* ... OB3 (7 – *n*) H-bonds, a bonding scheme comparable to that of β-cyclodextrin dimeric complexes [8], with average distance 2.80(6) Å (range 2.71 – 2.85 Å). The angles CA3*n* —OA3*n* ... OB3(7 – *n*) and OA3*n* ... OB3(7 – *n*)—CB3(7 – *n*) have mean values 117(4)° (range 112.6 – 121.5°) and 116(4)° (range 110.2 – 119.9°) respectively. The lateral shifting of the centers of the αCD monomers in the dimer is very small (0.2 Å). The dimers do not stack on top of each other to form channels, forming an angle of 21° with the **b** axis (Fig. 2). The packing rather resembles the Intermediate packing mode of βCD complexes [8] with the centers of consecutive dimers laterally shifted by 6 Å.

One diamine molecule, very well localized, spans the dimer cavity along its axis. The

TABLE I Crystal data and structure refinement

Molecular formula	$(C_{36}H_{60}O_{30})_2 \cdot C_{12}H_{28}N_2 \cdot (H_2O)_{14.4}$
Formula weight	2397
Temperature	293 K
Radiation/Wavelength	0.71070 Å
Space group	$P2_1$
a, *b*, *c*	14.10(2), 16.91(2), 24.45(4) Å
β	97.40(3)°
Volume/Z	5781(14) $Å^3$/2
Density (calculated)	1.398 g/cm^3
2θ range for data collection	0 – 41°
Index ranges	$-13 \leq h \leq 13, -16 \leq k \leq 0, 0 \leq l \leq 23$
Reflections collected/independent [*R*(int) = 0.0127]	5723/5559
Solution method	Molecular replacement [14]
Refinement method	Full matrix least squares on F^2
Data/restraints/parameters	5552/26/856
Goodness of fit of F^2	1.050
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.075$ $wR^2 = 0.201$
R indices (all data)	$R = 0.091$ $wR^2 = 0.227$
Largest diff. peak and hole	0.517 and $-0.464\,e\,Å^{-3}$

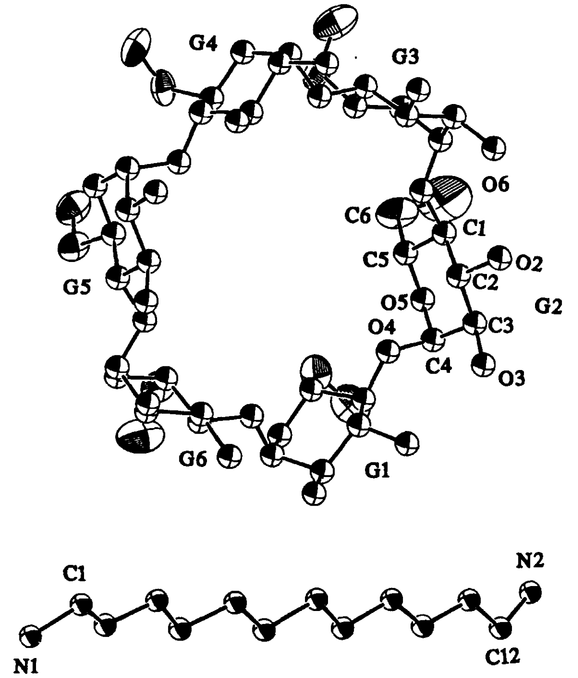

FIGURE 1 Atom numbering scheme for host and guest atoms. Displacement ellipsoids are plotted at the 50% level.

TABLE II α-Cyclodextrin macrocycle characteristics

Residue	D^a	φ^b	d^c	α^d	D_3^e
Molecule A					
G1	4.24	120.8	−0.02	83	2.85
G2	4.20	120.7	0.03	83	2.85
G3	4.23	118.9	−0.01	80	2.94
G4	4.19	119.9	−0.02	84	2.81
G5	4.26	121.3	0.03	85	2.80
G6	4.14	118.4	−0.02	83	2.85
Molecule B					
G1	4.18	117.9	0.01	83	2.87
G2	4.20	120.2	−0.01	85	2.83
G3	4.24	123.1	0.01	84	2.80
G4	4.21	117.1	−0.00	82	3.00
G5	4.29	119.8	−0.00	79	3.04
G6	4.23	121.8	−0.00	78	2.91

[a] Distances between atoms O4*n*... O4(*n* + 1).

[b] Angles between atoms O4(*n* − 1)... O4*n*... O4(*n* + 1).

[c] Deviations (Å) from the least-squares optimum plane of the six O4*n* atoms.

[d] Dihedral angle between the O4*n* plane and optimum planes through C2*n*, C3*n*, C5*n* and O5*n*.

[e] Intramolecular hydrogen-bond distances between atoms O3*n*... O2(*n* + 1).

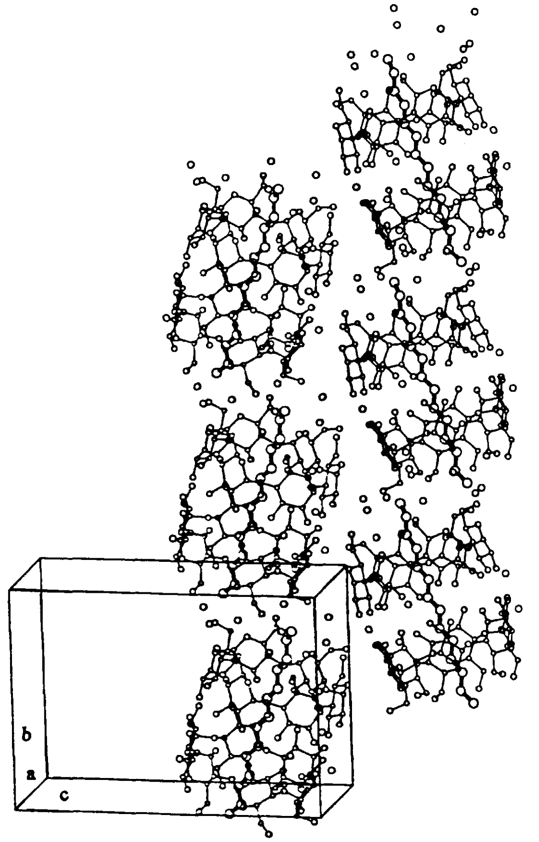

FIGURE 2 The packing of the dimeric complex molecules.

nitrogen atoms protrude from the primary hydroxyl sides and hydrogen-bond directly to two primary hydroxyl oxygen atoms of consecutive dimers: N1... OB61 2.99(3) Å and N2... OA62 2.64(3) Å, where atoms OB61 and N1 as well as OA62 and N2 belong to consecutive dimeric complexes. Atom N1 is also H-bonded to W174 (N1... W174 3.05(4) Å) (Fig. 3).

Comparison with Other Dimeric Complexes

A search in the Crystallographic Cambridge Database [9] provided us with the coordinates of nine structures of dimeric αCD complexes with reference codes CYDXLI [4], JEHYIE [10], JEMGUD [11], KIWYUK [3], KIWZEV [3], KOGKEW [6], PEPBUH [12], KOGKIA [6] and ZZZANG10 [4] (Tab. III).

The first seven are isomorphous. They belong to space group P1 and the mean values of their cell

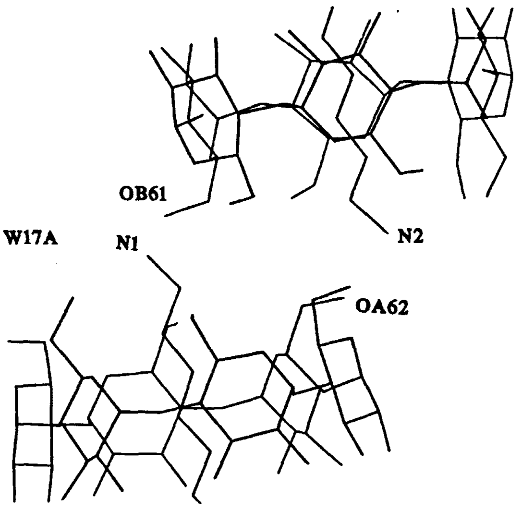

FIGURE 3 Detail of the hydrogen-bonded nitrogen atoms of the guest molecules (OB61, OA62 are primary hydroxyl oxygen atoms of the host, W17A is a water oxygen atom.

dimensions are $a = 13.83(5)$, $b = 13.88(3)$, $c = 15.62(6)$ Å, $\alpha = 93(1)$, $\beta = 87(3)$ and $\gamma = 119.9(3)$°. The dimers align along the crystallographic **c** axis forming channels. In all of them the macrocycles comprising the dimer, though almost parallel, are laterally shifted to each other. In CYDXLI, KIWZEV, KOGKEW and KOGKIA the shifts were calculated to be 1.1, 1.2, 1.2 and 1.25 Å, respectively. The distortion of the dimeric cavity is attributed to the guest dimensions. Apart from CYDXLI, in which the guest is lithium triiodide, in JEHYIE, JEMGUD, KIWYUK, KIWZEV, KOGKEW and PEPBUH, the guest molecules are metallocenes of transition metal elements where the ligands are n^5-C_5H_5 (JEMGUD, KIWYUK, KIWZEV), n^5-C_5H_5/C_7H_8 (KOGKEW) or n^5-C_5H_5/C_6H_6 (PEPBUH). In all cases the metal complex is encapsulated within the cavity of the dimer with the metal atom (or ion) situated close to its center. This kind of accommodation requires the extra space provided by the macrocycles' shifting. An immediate result of that shifting is the distortion of the regular OA3n ... OB3($7-n$) H-bonding scheme within the dimer, mentioned above for the present complex. The new H-bonding scheme comprises several OA3n... OB3n, OA(B)2n... OB(A)3n and OA(B)2n... OB (A)2n H-bonds with no regularity.

KOGKIA crystallizes in $P3_2$ and represents a series of αCD adducts (mean cell dimensions $a = 13.85(3)$ $c = 50.2(3)$ Å), where the guest is also a metallocene, but various substituents have been introduced into the ring ligands or the ring ligands are bridged. The resulting increase in the size of the guest demands an enlarged cavity which is accomplished by the non-parallel positioning of the αCD macrocycles. Thus, the latter form an angle of 15° and they are laterally shifted by 1.25 Å with respect to each other. However, despite the distortion, the dimeric complexes align along **c** axis and form channels.

ZZZANG10 crystallizes in $P4_22_12$ with cell dimensions $a = 19.93$ and $c = 30.88$ Å. As in the title complex (ADA), the αCD monomers are not shifted relative to each other and the dimer is undistorted. The same regularity of the H-bonding scheme is observed: the average distance OA3n... OB3($7-n$) is 2.84(9) Å and the angles CA3n—OA3n... OB3($7-n$) and OA3n... OB3($7-n$)—CB3($7-n$) have average values 117(1) and 111(3)° respectively. The identical geometry of the dimers of ZZZANG10 and ADA clearly explains why the Patterson search methods (described in the experimental part) applied to ADA data worked with only the cyclodextrin skeleton of ZZZANG10 as a searching model.

Despite the similarity of the dimers, the packing of the two complexes differs. In ZZZANG10 the dimers are arranged in channels parallel to the **c** axis, as in all the so far reported αCD dimeric structures, whereas in the present structure, the dimers are isolated (Fig. 2). This difference is attributed to the shape and size of 1,12-diaminododecane. We believe that in the case of the bulky guests situated in the center of the dimer, the primary faces are free to self-associate and form channels. Polyiodides also do not interfere with formation of channels since their existence depends upon it. On the contrary, 1,12-diaminododecane is a molecule with H-bond forming terminal groups and long

TABLE III α-Cyclodextrin dimeric structures

Space group	Reference Code [9]	αCD complexed with	Reference
	CYDXLI	Lithium polyiodide	[4]
	JEHYIE	(η^6-Benzene)-(η^5-cyclopentadienyl) iron hexafluorophospate	[10]
P1	JEMGUD	Ferrocene	[11]
	KIWYUK	Ferrocenium hexafluorophosphate	[3]
	KIWZEV	Rhodiocenium hexafluorophosphate	[3]
	KOGKEW	(η^5-Cyclopentadienyl)-(η^6-cycloheptatrienyl) iron hexafluorophosphate	[6]
	PEPBUH	(η^6-Benzene)-(η^5-cyclopentadienyl) ruthenium hexafluorophosphate	[12]
$P3_2$	KOGKIA	(η^5-Cyclopentadienyl)-(η^5-indan) iron hexafluorophosphate	[6]
$P4_22_12$	ZZZANG10	Cadmium polyiodide	[4]
$P2_1$		1,12-Diaminododecane (ADA)	present structure
$P2_12_12_1$		12-Aminododecanoic acid	[1c]

enough to allow those groups to protrude from the primary faces of the dimer. Thus, the terminal amino groups H-bond to neighboring hydroxyl groups, not only forbidding any self-association of the host dimers, but inducing their relative shifting (Fig. 3). Therefore, the present complex is a characteristic case where the guest clearly affects the primary faces of cyclodextrin dimers and influences their packing.

MATERIALS AND METHODS

Preparation and Crystallization of the Complex

1,12-diaminododecane was added in a 0.07 M aqueous solution of αCD at a host to guest ratio of 2:1. After the mixture was stirred under mild heating (50°C), the complex precipitated as a white powder which was readily redissolved by slight dilution, addition of some drops of ethanol and heating to 55°C. Colorless crystals were formed by cooling the solution slowly over a four-day period up to 10°C.

X-ray Structural Analysis

A single crystal (0.7 × 0.5 × 0.3 mm) of the complex, sealed in a glass capillary in the presence of mother liquor, was used for data collection with a Crystal Logic diffractometer [13]. Cell parameters were determined by 16 reflections in the range $11 < 2\theta < 23°$. Intensity data were collected with Nb-filtered MoKα radiation with θ—2θ scan mode up to 41° in 2θ. The scan speed was 4° min^{-1} for $2\theta < 36°$ and 3° min^{-1} for $36 < 2\theta < 41°$. The decay of the crystals was monitored by 3 standard reflections which did not show any decrease in intensity during data collection.

The structure is non-isomorphous to any of the so far reported αCD complexes. The cell volume and the space group symmetry indicated that the asymmetric unit must contain one αCD dimer. Firstly, the cyclodextrin skeleton (C1, C2, C3, C4, C5, O5 atoms) of a distorted dimer (Rhodiocenium hexafluorophosphate) [3] was used as a structural model to try Patterson search methods (program PATSEE) [14] with no success. However, when the skeleton atoms of the undistorted dimer (αCD-cadmium polyiodide) [4] was tried, a model suitable for initial phasing resulted. Subsequent difference electron density maps, produced by Shelxl93 [15], revealed the missing atoms of the αCD host, the guest and water molecules. Hydrogen atoms were calculated for all C atoms by using a riding model with Ueq(H) equal to 1.2Ueq of the parent C atoms. Anisotropic displacement parameters were assigned to all C6, O6 and to the water O atoms (except for two disordered). The guest molecule was refined isotropically by using geometrical constraints based on the published structure of 1,12-diaminododecane [16].

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References

[1] (a) Rontoyianni, A. and Mavridis, I. M. (1996). *Acta Cryst.*, **C52**, 2277; (b) Mentzafos, D.; Mavridis, I. M.; Schenk, H. (1994). **253**, 39; (c) Rontoyianni, A. and Mavridis, I. M. In: *17th European Crystallographic Meeting* (1997). Lisbon, Portugal, 24–28 August, book of abstracts, p. 100.

[2] Philp, D. and Stoddart, J. F. (1996). *Angew. Chem. Int. Ed. Engl.*, **35**, 1154.

[3] Klingert, B. and Rihs, G. (1991). *J. Inc. Phen.*, **10**, 255.

[4] Noltemeyer, M. and Saenger, W. (1980). *J. Am. Chem. Soc.*, **102**, 2710.

[5] Nicolis, I., Villain, F., Coleman, A. W. and de Rango, C. (1992). *Supramol. Chem.*, **3**, 251.

[6] Klingert, B. and Rihs, G. (1991). *J. Chem. Soc. Dalton Trans.*, p. 2749.

[7] Rontoyianni, A. and Mavridis, I. M., unpublished results.

[8] Mentzafos, D., Mavridis, I. M., Le Bas, G. and Tsoucaris, G. (1991). *Acta Cryst.*, **B47**, 746.

[9] *Cambridge Structural Database System*, V 5.12.

[10] Klingert, B. and Rihs, G. (1990). *Organomettalics*, **9**, 1135.

[11] Odagaki, Y., Hirotsu, K., Higuchi, T., Harada, A., Takahashi, S. (1990). *J. Chem. Soc. Dalton Trans. 1*, p. 1230.

[12] Meister, G., Stoeckli-Evans, H. and Suss-Fink, G. (1993). *J. Organomet. Chem.*, **453**, 249.

[13] C. Strause, unpublished results.

[14] Egert, E. and Sheldrick, G. M. (1985). PATSEE. "Search for a Fragment of Known Geometry by Integrated Patterson and Direct methods", *Acta Cryst.*, **A41**, 262.

[15] Sheldrick, G. M. (1993). SHELXL93. *Program for the Refinement of Crystal Structures*. University of Göttingeng, Germany.

[16] Mc Neil, R., Scheidt, W. R. and Thomas, J. K. (1981). *Mol. Cryst. Liq. Cryst.*, **78**, 85.