Electronic Supplementary Material for CrystEngComm

A novel packing of *β*-Cyclodextrin enclosing an unusual organization of guest: The inclusion complexes *β*-Cyclodextrin/4-pyridinealdazine.

Spyros D. Chatziefthimiou, Konstantina Yannakopoulou and Irene M. Mavridis*

Institute of Physical Chemistry, National Center for Scientific Research

"Demokritos", Aghia Paraskevi 153 10, Athens, Greece

SUPPORTING INFORMATION

*Corresponding author's e-mail: mavridi@chem.demokritos.gr

Table S1. Conformations of the macrocycle and the glucose units

Residue	D[a] (Å)	φ[b] (°)	d[c] (Å)	Tilt angles[d] (°)	D_3[e] (Å)	Torsion Angle(°) O5n-C5n-C6n-O6n
Molecule A						
G1	4.219 (7)	125.0 (2)	0.034 (4)	11.9 (2)	2.730 (8)	-54.8 (7) 59.8 (17)
G2	4.340 (8)	124.6 (2)	-0.012 (4)	10.3 (1)	2.822 (8)	-60.2 (8)
G3	4.472 (8)	132.6 (2)	-0.056 (4)	10.5 (1)	2.795 (9)	-66.3 (10)
G4	4.287 (8)	132.1 (2)	0.057 (4)	8.2 (2)	2.798 (9)	-65.4 (11) 60.0 (14)
G5	4.222 (8)	121.9 (2)	0.021 (4)	7.6 (2)	2.706 (8)	-62.9 (8)
G6	4.472 (8)	128.8 (2)	-0.069 (4)	7.3 (2)	2.767 (8)	-70.6 (10) 35.4 (14)
G7	4.392 (7)	135.0 (2)	0.025 (4)	10.3 (2)	2.783 (8)	74.9 (9)
Molecule B						
G1	4.242 (8)	130.4 (1)	0.083 (3)	9.8 (2)	2.690 (7)	-60.7 (7)
G2	4.332 (7)	122.4 (1)	-0.037 (3)	14.8 (2)	2.793 (8)	-57.5 (8)
G3	4.362 (7)	131.7 (2)	-0.057 (3)	6.7 (1)	2.855 (8)	-62. (7)
G4	4.378 (7)	129.5 (2)	0.042 (3)	11.6 (2)	2.786 (7)	-65.6 (7)
G5	4.360 (7)	129.6 (1)	0.057 (3)	10.3 (2)	2.774 (7)	73.1 (9) -60.0 (1)
G6	4.195 (7)	122.6 (2)	-0.088 (3)	14.4 (2)	2.813 (8)	61.4 (8)
G7	4.580 (7)	133.5 (2)	-0.001 (3)	7.0 (2)	2.856 (8)	-62.6 (7)
Molecule C						
G1	4.166 (8)	123.5 (2)	0.159 (3)	11.7 (2)	2.690 (9)	-62.0 (7)
G2	4.452 (8)	129.4 (2)	-0.018 (4)	16.8 (2)	2.805 (7)	65.3 (8)
G3	4.318 (7)	129.5 (2)	-0.132 (4)	5.6 (1)	2.815 (8)	-56.4 (8)
G4	4.374 (7)	129.9 (2)	0.035 (4)	13.1 (2)	2.762 (8)	-64.7 (8)
G5	4.200 (8)	124.3 (2)	0.178 (4)	8.1 (2)	2.704 (7)	77.8 (9)
G6	4.382 (8)	129.8 (2)	-0.174 (4)	17.1 (3)	2.751 (8)	71.8 (9)
G7	4.411 (7)	132.6 (2)	-0.048 (4)	7.2 (1)	2.831 (10)	-63.1 (8)

[a]O4n…O4(n+1) distances; [b]O4(n-1)…O4n…O4(n+1) angles; [c]Deviations (Å) from the least-squares optimum plane of the seven O4n atoms; [d]Tilt angles between the optimum O4n plane and the mean planes through atoms O4(n-1), C1n, C4n, O4n (with esds in parentheses). [e] Intramolecular hydrogen-bond distances between atoms O2n…O3(n-1)

Table S2. Ring Puckering Analysis (Cremer, D.; Pople J. A. *J. Am. Chem. Soc*. **1975**, *97*, 1354-1358**;** e.s.d. following Norrestam, Acta Crystallog.**1981**, A37, 764-765)

Residue	Q	Θ	φ
Molecule A			
G1	0.575(8)	5.8(8)	151(8)
G2	0.563(8)	4.2(8)	88(9)
G3	0.567(8)	0.6(8)	343(18)
G4	0.572(9)	6.0(8)	191(8)
G5	0.560(8)	3.3(8)	116(13)
G6	0.559(8)	5.1(9)	80(8)
G7	0.586(8)	5.5(8)	255(8)
Molecule B			
G1	0.579(8)	8.1(8)	242(5)
G2	0.570(8)	2.1(8)	76(23)
G3	0.591(8)	3.5(7)	164(12)
G4	0.563(8)	2.6(8)	130(16)
G5	0.557(8)	3.3(7)	171(13)
G6	0.554(7)	1.9(7)	20(26)
G7	0.564(8)	6.3(8)	106(7)
Molecule C			
G1	0.579(8)	4.6(8)	241(10)
G2	0.540(8)	7.3(8)	59(6)
G3	0.564(8)	4.4(7)	331(9)
G4	0.547(8)	3.9(7)	330(11)
G5	0.558(8)	2.3(8)	310(25)
G6	0.564(8)	5.9(9)	76(9)
G7	0.553(8)	2.7(8)	325(17)

Table S3. Intermolecular hydrogen bonds between macrocycles

a. Between hosts A … B (dimer)				
O_a…O_b	**Distance (Å)**	**C_a-O_a…O_b (^{o})**	**O_a…O_b-C_b (^{o})**	**Symmetry Operation**
O31A - O37B	2.704 (0.0074)	117.6 (4)	115.9 (4)	Along the channel
O32A - O36B	2.777 (0.0073)	118.6 (4)	115.8 (4)	Along the channel
O33A - O35B	2.766 (0.0070)	113.0 (4)	119.6 (4)	Along the channel
O34A - O34B	2.787 (0.0074)	121.3 (5)	110.3 (4)	Along the channel

O35A - O33B	2.696 (0.0071)	113.3 (4)	119.9 (4)	Along the channel
O36A - O32B	2.863 (0.0076)	123.0 (5)	113.4 (4)	Along the channel
O37A - O31B	2.808 (0.0075)	115.5 (5)	116.5 (4)	Along the channel
b. Between hosts A … C				
O_a…O_c	**Distance (Å)**	**C_a-O_a…O_c (^{o})**	**O_c…O_a-C_a (^{o})**	**Symmetry Operation**
O61A_b - O31C	2.690 (32)	115.9 (17)	111.8 (8)	Intra-trimer
O63A - O33C	2.668 (8)	98.1 (6)	133.5 (5)	Along the channel
O64A_a - O34C	2.866 (9)	109.3 (7)	122.5 (4)	Along the channel
O64A_b - O24C	3.007 (20)	116.7 (12)	113.8 (6)	Along the channel
O66A_b - O36C	2.780 (25)	122.4 (14)	111.7 (7)	Along the channel
O65A - O35C	3.189 (8)	83.8 (4)	137.5 (4)	Along the channel
O67A - O37C	2.741 (10)	95.4 (6)	114.7 (5)	Along the channel
c. Between hosts C … B				
O_c…O_b	**Distance (Å)**	**C_c-O_c…O_b (^{o})**	**O_b…O_c-C_c (^{o})**	**Symmetry Operation**
O62C - O66B	2.791 (9)	134.8 (6)	89.7 (4)	x, y, z+1
O64C - O64B	2.751 (7)	103.6 (4)	100.2 (4)	x, y, z+1
Intermolecular hydrogen bonds of the hosts (A, B, and C) among the columns				
O_a…O_b	**Distance (Å)**	**C_a-O_a…O_b (^{o})**	**O_a…O_b-C_b (^{o})**	**Symmetry Operation**
O61A_a - O25C_	2.592 (9)	129.4 (5)	99.3 (4)	x, y+1, z
O61A_a - O65A	2.973 (10)	135.1 (5)	118.5 (5)	x, y+1,+z
O25A - O27B	2.700 (8)	107.1 (4)	109.6 (4)	x, y-1,+z
O63B - O67B	2.854 (7)	127.9 (4)	110.1 (4)	x, y-1,+z
O27A - O25B	2.715 (8)	93.8 (4)	120.3 (4)	x-1, y,+z
O61C - O63B	2.633 (7)	108.1 (4)	107.1 (4)	x, y+1, z+1
O63C - O61B	2.702 (8)	105.3 (4)	108.5 (4)	x+1, y, z+1
O54C - O61B	3.187 (8)	133.7 (4)	143.4 (5)	x+1, y, z+1
O61B - O63C	2.702 (8)	108.5 (4)	105.3 (4)	x-1, y, z-1
O51B - O63C	3.176 (7)	112.6 (4)	1295 (4)	x-1, y, z-1
O63B - O51C	3.001 (7)	128.2 (4)	112.9 (4)	x, y-1,+z-1
O54B - O61C	3.100 (8)	112.9 (4)	150.6 (4)	x, y-1, z-1

Table S4. Selected H-bonds distances in the guest-water assembly (a and b refer to molecules of major and minor occupancies, respectively).

$Guest_a$ - O_{water}	**Distance**	**$Guest_b$ - O_{water}**	**Distance**
N1_1a -O20	2.74 (1)	N1_1b -O20	2.97 (2)
N1_2a -O29	2.88 (1)	N1_2b - O29	2.87 (3)
N4_1a - O33	2.94 (2)	N4_1b -O33	2.95 (2)
N4_1a - O36_a	3.53 (3)	N4_1b - O36_a	2.93 (2)
N4_2a - O36_a	3.37 (3)	N4_2b - O36_a	2.74 (4)
N4_2a - O36_b	3.03 (2)	N4_2b - O36_b	2.98 (4)
N4_2a - O35	2.68 (2)	N4_2b - O35	3.04 (4)
O_{water} - O_{water}	**Distance**	**O_{water} - O_{water}**	**Distance**
O16 - O20	2.77 (1)	O24 - O27_a	2.77 (3)
O16 - O22_a	2.69(1)	O27_a - O35	2.66 (2)
O16 - O22_b	2.91(1)	O33 - O35	2.55 (2)
O19 - O29	2.70 (1)	O33 - O36_b	2.83 (4)
O20 - O24	2.78 (1)	O33 - O36_a	2.19 (3)
O20 - O29	2.73 (1)	O33 - O41_b	2.70 (4)
O22_a - O36_a	2.622 (2)	O33 - O41_a	2.86 (5)
O22_b - O36_b	2.14 (5)	O35 - O41_a	2.86 (5)

Table S5. H-Bonds between water molecules and CD macrocycles

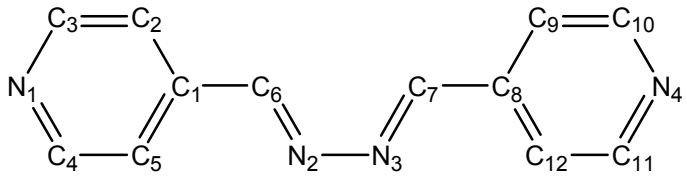
O_{cd}…O_{water}	**Distance (Å)**	**C_{cd}-O_{cd}…O_{water} (^{o})**	**Symmetry Operation**
O21A-O42	2.412 (38)	103.0 (9)	x, y-1, z
O61A_a-O13	2.703 (9)	104.9 (5)	
O32A-O34_a	2.818 (18)	124.2 (7)	x-1, y-1, z
O62A-O39_a	2.739 (21)	141.0 (6)	
O62A-O3	2.755 (9)	111.4 (5)	
O62A-O15	2.718 (9)	117.0 (6)	
O23A-O25	2.690 (11)	103.4 (5)	
O63A-O31	2.452 (15)	130.8 (8)	
O63A-O32	2.866 (23)	131.2 (7)	x-1, y, z
O34A-O30_b	2.829 (39)	117.0 (10)	x, y+1, z
O34A-O30_a	3.000 (15)	137.4 (6)	x, y+1, z
O54A-O37_a	2.846 (16)	104.0 (5)	x, y+1, z
O64A_a-O37_a	2.884 (15)	107.5 (5)	
O35A-O42	2.822 (37)	111.8 (8)	
O65A-O28_a	2.729 (15)	114.5 (6)	x+1, y+1, z
O65A-O28_b	2.682 (26)	128.7 (8)	x+1, y+1, z
O26A-O9_b	2.742 (40)	124.3 (9)	x+1, y+1, z
O36A-O23_b	2.862 (19)	131.9 (6)	
O66A_a-O37_a	3.078 (15)	126.9 (6)	
O66A_b-O38_a	3.058 (15)	107.1 (7)	
O66A_a-O40	3.038 (28)	137.5 (12)	
O57A-O32	2.885 (15)	118.9 (5)	
O21B-O26	2.597 (10)	115.7 (5)	x+1, y, z
O61B-O7	2.780 (8)	99.5 (5)	x+1, y, z+1

O22B-O23_a	2.650 (10)	109.5 (5)	
O32B-O5	2.953 (8)	117.4 (4)	x+1, y+1, z+1
O52B-O7	2.808 (7)	124.7 (4)	x+1,+y,+z+1
O62B-O8	2.668 (9)	111.0 (5)	x+1, y+1, z+1
O62B-O2	2.782 (8)	109.3 (4)	x+1, y+1, z+1
O23B-O17	2.699 (9)	104.7 (5)	x+1, y+1, z+1
O24B-O30_a	2.728 (13)	103.6 (5)	x, y+1, z
O34B-O23_b	2.915 (19)	111.2 (6)	x-1, y, z
O34B-O23_a	2.734 (11)	107.0 (5)	x-1, y, z
O64B-O4	2.765 (8)	118.0 (4)	x, y+1, z+1
O35B-O26	2.784 (9)	109.8 (4)	
O65B_b-O14	2.806 (21)	126.1 (12)	x, y, z-1
O65B_a-O41_b	2.841 (13)	103.2 (5)	
O65B_a-O41_a	2.614 (14)	133.9 (5)	
O26B-O9_a	2.682 (10)	102.2 (4)	
O36B-O30_a	2.744 (12)	127.6 (5)	
O66B-O22_b	2.779 (38)	123.7 (10)	x, y, z+1
O66B-O22_a	2.814 (11)	107.2 (5)	x, y, z+1
O66B-O24	2.859 (11)	111.4 (4)	
O37B-O17	2.959 (9)	115.6 (4)	x+1, y, z+1
O67B-O6	2.725 (7)	118.8 (4)	x+1, y, z+1
O21C-O13	2.674 (0.0083)	121.3 (4)	
O61C-O4	2.755 (8)	100.4 (4)	
O22C-O3	2.710 (7)	110.9 (4)	
O32C-O2	2.821 (8)	111.5 (4)	
O52C-O4	2.837 (8)	129.7 (4)	
O62C-O5	2.988 (9)	100.2 (5)	
O23C-O18	2.659 (9)	104.0 (5)	
O53C-O6	3.282 (8)	110.0 (4)	
O63C-O6	2.847 (8)	100.1 (5)	
O24C-O37_b	2.581 (25)	100.2 (7)	x, y+1, z
O24C-O37_a	2.769 (17)	135.0 (8)	x, y+1, z
O34C-O3	2.821 (8)	110.5 (4)	x, y+1, z
O54C-O7	2.925 (8)	113.7 (4)	
O64C-O7	2.706 (7)	117.3 (4)	
O35C-O13	2.703 (9)	112.4 (4)	x, y+1, z
O65C-O19	2.743 (10)	99.2 (5)	x, y, z-1
O65C-O27_a	2.684 (13)	104.2 (6)	
O26C-O38_a	2.944 (17)	117.8 (7)	x+1, y+1, z
O26C-O15	2.701 (8)	108.7 (4)	1+x , 1+y,z
O36C-O38_a	3.138 (28)	115.5 (6)	x+1, y+1, z
O36C-O39_a	2.864 (21)	128.1 (7)	x+1, y+1, z
O66C-O16	2.654 (10)	109.4 (6)	x, y, z-1
O66C-O19	2.706 (10)	139.9 (6)	x, y, z-1
O66C-O27_a	2.992 (14)	122.3 (5)	

Table S6. Crystallographic data

Empirical formula	C150 H165.28 N8 O142.05
Formula weight	4352.98

Temperature	100(2) K
Wavelength	0.80150 Å
Crystal system, space group	Triclinic, P 1
Unit cell dimensions	a = 15.067(10) Å, alpha = 101.02(6) deg.
	b = 15.478(7) Å, beta = 99.84(8) deg
	c = 23.36(2) Å, gamma = 105.10(4) deg.
Volume	5021(26) Å^3
Z, Calculated density	1, 1.440 g/cm^3
Absorption coefficient	0.131 mm^-1
F(000)	2258
Crystal size	0.4 x 0.4 x 0.3 mm
Theta range for data collection	1.59 to 27.43 deg
Limiting indices	0<=h<=17, -17<=k<=17, -26<=l<=26
Reflections collected / unique	14599 / 14599 [R(int) = 0.0000]
Completeness to theta = 27.43	91.5 %
Refinement method	Full-matrix least-squares on F^2
All data /data [Fo > 4sig(Fo)]/ restraints / parameters	14599 /13814/ 363 / 2791
Goodness-of-fit on F^2	1.037
Final R indices [Fo > 4sig(Fo)]	R1 = 0.0653, wR2 = 0.1772
R indices (all data)	R1 = 0.0681, wR2 = 0.1804
Absolute structure parameter	0.6(9)
Largest diff. peak and hole	0.560 and -0.427 e.Å^-3



Scheme 1. Numbering scheme of 4-pyridinealdazine. Major occupancy guests **1a** and **2a**. Minor occupancy guests **1b** and **2b**.

Table S7. Structural characteristics of the guest dimers.

Major occupancy guests **1a** and **2a**. Minor occupancy guests **1b** and **2b**.	**1a – 2a**	**1b - 2b**
Angle between the two guest molecules	16.8° (4)	6.4° (6)
Angle between the rings (C_1-C_2-N_1-C_3-C_4-C_5) of the dimer	14.7° (3)	13.8° (6)
Angle between the rings (C_8-C_9-N_4-C_{10}-C_{11}-C_{12}) of the dimer	18.0° (5)	2.6° (6)

Smallest π...π distance	3.233 (8) Å (C9_1 – C8_2)	3.286 (7) Å (C5_1 – C2_2)
Distances between the centers of the (C_1-C_2-N_1-C_3-C_4-C_5) rings of the dimer	3.726 (11)Å	3.600 (11)Å
Distances between the centers of the (C_8-C_9-N_4-C_{10}-C_{11}-C_{12}) rings of the dimer	3.726 (11)Å	3.453 (10)Å

Table S8. Intermolecular interactions between βCD and guest dimers

CD molecule	Guest molecule	Distance (Å)
O61A_a	C8_1a	3.55 (1)
O61A_b	C9_1a	3.23 (1)
C51A	C7_1a	3.59 (2)
C36A	C2_2a	3.48 (1)
O67A	C7_2a	3.40 (2)
O44A	N2_2b	3.66 (3)
O45A	N2_2a	3.52 (1)
C36B	C4_1a	3.65 (2)
C37B	N1_1a	3.80 (2)
C37B	C4_1b	3.60 (3)
O46B	N1_1a	3.70 (1)
O46B	N1_1b	3.81 (2)
C31C	N4_1b	3.58 (2)
O41C	N4_1a	3.82 (2)
O41C	N4_1b	3.79 (2)
O45C	N4_2a	3.89 (2)
O45C	N4_2b	3.85 (4)
O27C	C9_2a	3.69 (1)