Supplementary Materials

Structural Elucidation of α-Cyclodextrin—Succinic Acid *Pseudo* Dodecahydrate: Expanding the Packing Types of α-Cyclodextrin Inclusion Complexes

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1. CSD Refcodes

The following is a list of all the recodes resulting of searching the CSD, V 5.36 including updates to November 2014, for structure of α-CD with 3-D coordinates. The refcodes were categorised according to the packing type described by Saenger and Steiner [1].

(a) Herringbone-type cage: ARACEB, BANXUJ, BOBPAK, BUPDEV, CDEXKR10, CDEXME10, CDEXTI10, CHXAMH, CHXAMH02 (redetermination, excluded), CHXAMH03, CHXAMH04 (redetermination, excluded), CYDXKR10, DAXTEB, DEGTEO, GEVTOQ, GULTUC, HOGCIP, LOVVAT, QERVUE, QOHMEF, RAXPOV, REGPAW, YENQAK.

(b) Brick-type cage: ACDHBA, ACDMFM, ACDMSM, ACDPNP, ACDPRO, BOBNUC, BOLVUT, BORYOX, CDEXIA01 (redetermination, excluded), CDEXIA10, CHAIPL, EJOVOO, GOQZUH, IFOBUB, INUPAI, INUPEM, MESYEO, PAZKOS, QENTIN, QENTOT, QIZMIW, RIRZUN (α-cycloaltrin, excluded), TUSHEV, TUSHIZ, VEHQAA, WEXKOZ, ZEJDEX.

(c) Channel type (pseudohexagonal and hexagonal/honeycomb): BAJJAX, BIJHOR, CAQPEP, CDNOAN, CIGLAG, CYDXLI10, JEHYIE, JEMGUD, JUMYOF, JUMYUL, KIRJOK10, KIWYUK, KIWZEV, KOBLOC, KOGKEW, KOGKIA, LIZQAO, MOVFUY, PEPBUH, PUPTEZ, QACCEE, QACCII, WEXLEQ, XIGBOE, YIHJOQ, YIHJUW, ZASYOH.

(d) Channel type (other): ACDMNP, ACDPRS, CAQPAL, CDKABA, CDXBZS, CDXKOM, CDXSOM, CHAMPA, EJOVUU, KEZGAZ, MESYAK, NIMROR, QOHMIJ, RAGZOO, SAQMII, TEXTEX, TEXTIB, WILJAC, WIZQEB, WUQKEZ, WUQKID, WUQKOJ, ZZZANG10.

2. Evolution of the Normalised Unit Cell Parameters as Function of Temperature

Normalised unit cell parameters are plotted against temperature (Figure 5 in the main paper). Data at 100 K were taken as a reference. To avoid the overlap of the error bars, T_c and T_V were shifted by +1 and −1 K, respectively. The uncertainty of the ratio $\sigma(a/a_0)$ was calculated using the equation of the propagation of uncertainty where:

$$\sigma\left(\frac{a}{a_0}\right) = \sqrt[2]{\left(\frac{\sigma a}{a}\right)^2 + \left(\frac{\sigma a_0}{a_0}\right)^2} \quad (1)$$

The same equation was used for generating $\sigma(c/c_0)$ and $\sigma(V/V_0)$.

Table S1. Crystallographic data of the multi-temperature structures of α-CD·SA inclusion complex.

Specimen	**Crystal 1**				**Crystal 2**			
***T*/K**	**90(2)**	**100(2)**	**120(2)**	**150(2)**	**180(2)**	**210(2)**	**240(2)**	**270(2)**
CCDC Number	**1437063**	**1437064**	**1437065**	**1437066**	**1437067**	**1437068**	**1437069**	**1437070**
Formula [a]	$C_{36}H_{60}O_{30}$, $C_4H_6O_4$, 12.09 H_2O	$C_{36}H_{60}O_{30}$, $C_4H_6O_4$, 12.14 H_2O	$C_{36}H_{60}O_{30}$, $C_4H_6O_4$, 12.14 (12.08) H_2O	$C_{36}H_{60}O_{30}$, $C_4H_6O_4$, 12.14 (11.54) H_2O	$C_{36}H_{60}O_{30}$, $C_4H_6O_4$, 12.14 (10.86) H_2O	$C_{36}H_{60}O_{30}$, $C_4H_6O_4$, 12.14 (10.27) H_2O	$C_{36}H_{60}O_{30}$, $C_4H_6O_4$, 12.14 (9.29) H_2O	$C_{36}H_{60}O_{30}$, $C_4H_6O_4$, 12.14 (7.87) H_2O
Crystal system	Trigonal				Trigonal			
Space group	*R*32				*R*32			
***a* = *b*/Å**	23.6625(6)	23.645(3)	23.6608(7)	23.6781(6)	23.6951(5)	23.7133(6)	23.738(13)	23.757(10)
***c*/Å**	55.7235(15)	55.706(7)	55.722(2)	55.7898(18)	55.8490(15)	55.8345(17)	55.76(3)	55.62(2)
α = β, γ/°	90, 120				90,120			
***V*/Å^3**	27020.3(16) Å3	26973(7) Å3	27015.8(19) Å3	27088.1(16) Å3	27155.8(14) Å3	27190.5(16) Å3	27212(34) Å3	27183(26) Å3
Z	18				18			
Z′	1				1			
***D*$_{calc}$/(g·cm^{-3})**	1.448	1.451	1.449	1.445	1.442	1.440	1.439	1.440
Meas./uniq./obs. reflections [b]	118804/11029/9149	45399/6390/5109	46751/6302/4512	47260/6315/4645	47564/6328/5099	47801/6347/5061	21178 */6034/3799	29882 */6297/3592
***d*$_{max}$/Å**	0.83	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Completeness to *d*$_{max}$	0.999	0.999	0.999	0.998	0.998	0.998	0.992	0.997
***R*$_{int}$**	0.0641	0.0752	0.1074	0.0988	0.0885	0.0877	0.0908	0.1253
Data/restraints/ parameters	11029/3989/1319	6390/3965/1247	6302/3971/1211	6315/3943/1201	6328/3895/1225	6347/3043/1147	6034/3038/1110	6297/1942/899
***R*$_1$** [c]	0.0467	0.0486	0.0566	0.0560	0.0689	0.0715	0.0723	0.0849
***wR*$_2$** [d]	0.1147	0.1043	0.1156	0.1188	0.1518	0.1644	0.1712	0.2111

[a] The number of water molecules indicated in brackets refers to the number of water molecules actually refined. This number underestimates the actual hydration number due to signal loss/thermal smearing of the electron density as temperature is increased. We don't think there is any reason for water loss, at least up to 240 K; hence, the reported formulae refer to the 100 K structure. This number was used to calculate all derived crystal properties; [b] Criteria for observed reflections: $I > 2\sigma(I)$; [c] ($F^2 > 2\sigma(F^2)$); [d] (F^2). * The marked decrease in the number of measured reflections at 240 K and 270 K is explained by a slight movement of the single crystal on the goniometer head at 240 K.

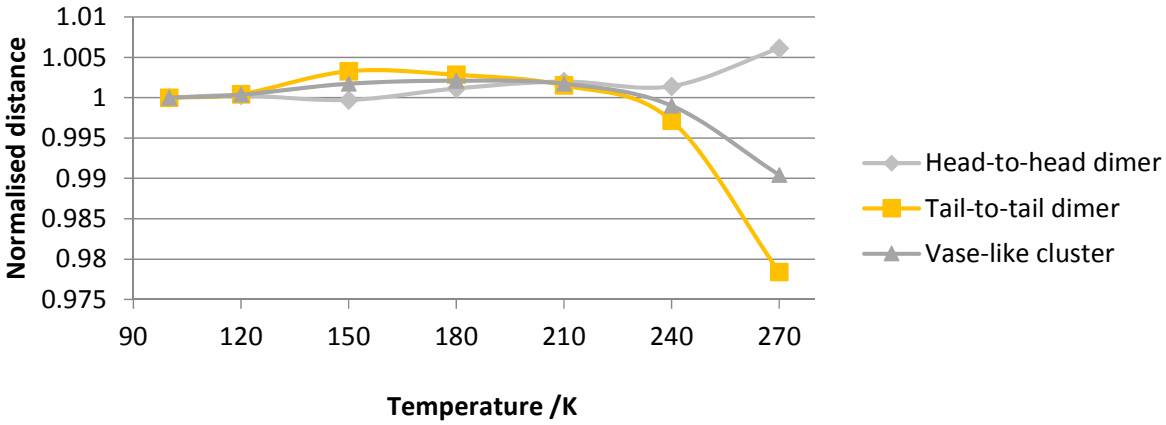


Figure S1. Evolution of the normalised distances between dimers in α-CD·SA. Distances were calculated based on the O(4) glycosidic planes using *MERCURY* [2].

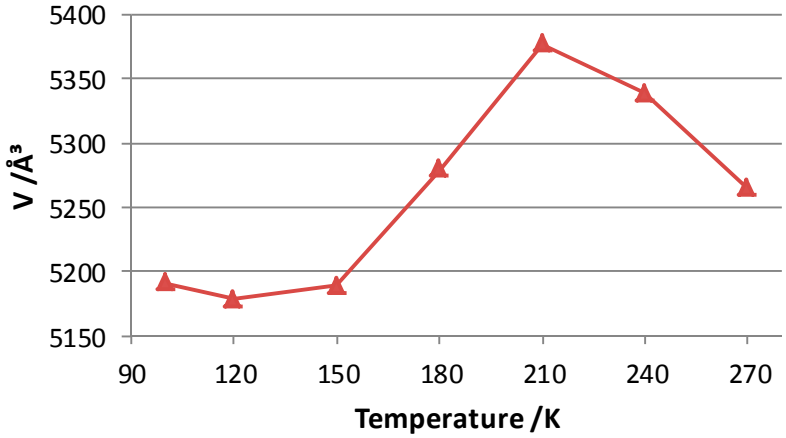
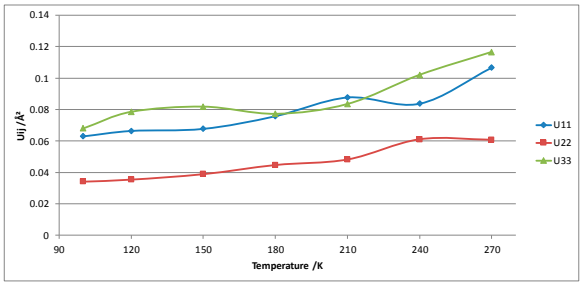
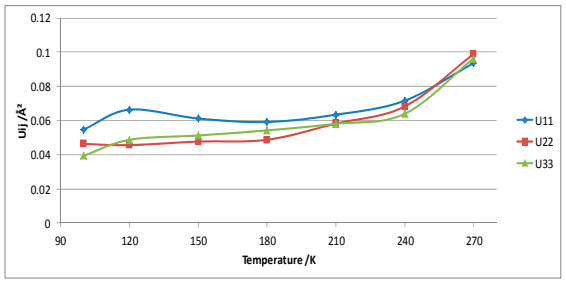


Figure S2. The solvent accessible void volume calculated using *MERCURY* [2] (grid spacing = 0.2 Å; probe radius = 1.2 Å).

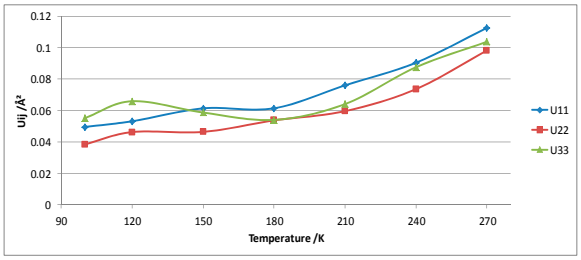
3. ADP Analysis



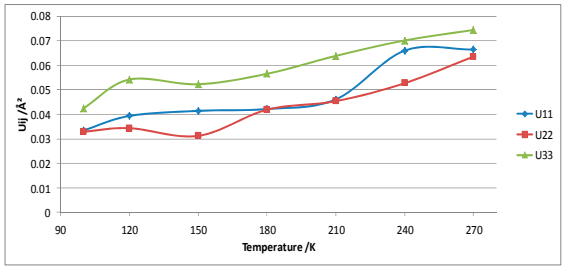
(**a**) **Water molecule O(1)_90**



(**b**) **Water molecule O(4)_91**

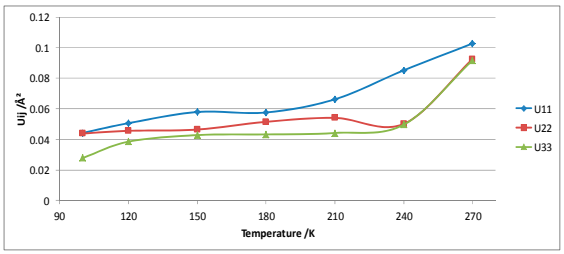


(**c**) **Water molecule O(2)_90**

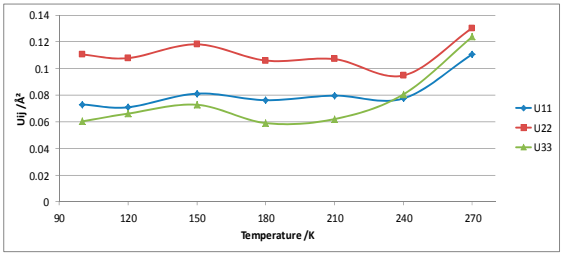


(**d**) **Water molecule O(5)_91**

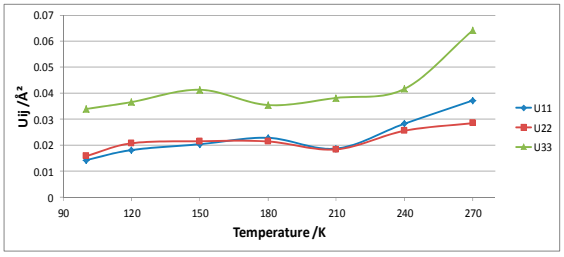
Figure S3. *Cont.*



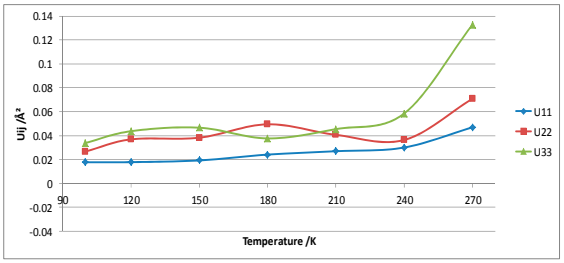
(e) **Water molecule O(3)_91**



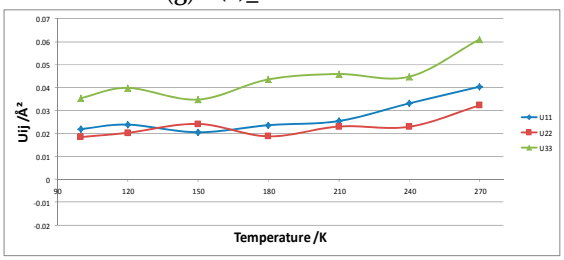
(f) **Water molecule O(6)_91**



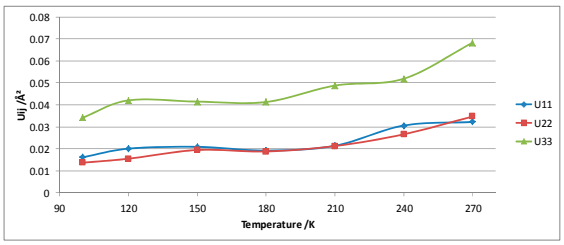
(g) **C(1)_11** of **A** α-CD



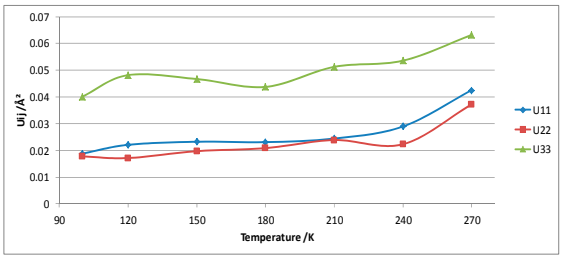
(h) **C(1)_31** of **C** α-CD



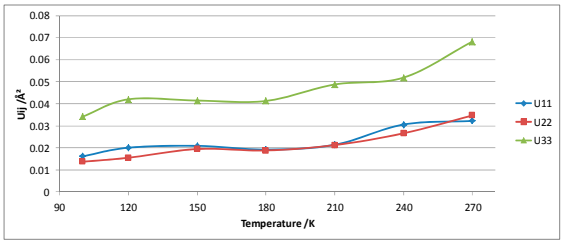
(i) **C(1)_21** of **B** α-CD



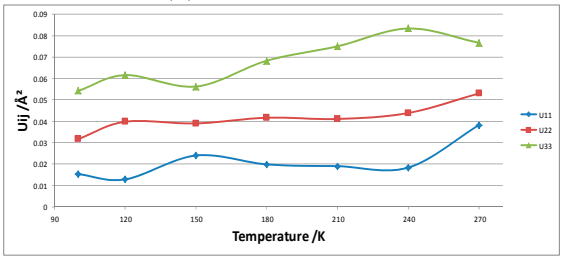
(j) **O(4)_11** of **A** α-CD



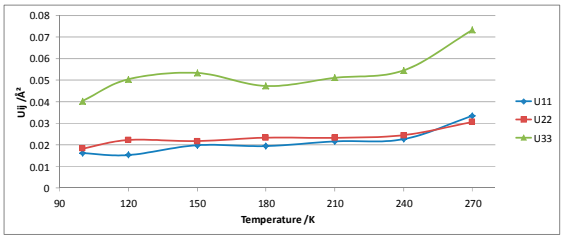
(k) **O(4)_22** of **B** α-CD



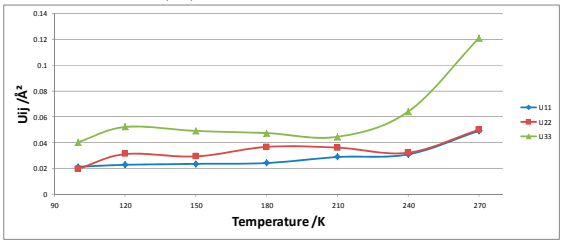
(l) **O(4)_12** of **A** α-CD



(m) **O(4)_31** of **C** α-CD



(n)**O(4)_21** of **B** α-CD



(o) O(4)_32 of **C** α-CD

Figure S3. U_{11}, U_{22} and U_{33} elements of the ADP tensor for selected atoms plotted as a function of temperature. The value of the ADPs were taken from the result file of the refinement of SHELX (res file). O(1) to O(6) are water molecules located in the interstices. The numbering suffix refers to the residue number in the structure.

References

1. Saenger, W.; Steiner, T. Cyclodextrin Inclusion Complexes : Host-Guest Interactions and Hydrogen-Bonding Networks. *Acta Crystallogr. Sect. A* **1998**, *54*, 798–805.
2. Macrae, C.F.; Bruno, I.J.; Chisholm, J.A.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A. Mercury CSD 2.0—New Features for the Visualization and Investigation of Crystal Structures. *J. Appl. Crystallogr.* **2008**, *41*, 466–470.