Electronic Supplementary Information (ESI)

Supramolecular complexes of α,α',δ,δ'-tetramethyl-cucurbit[6]uril binding with enantiomeric amino acids

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Experimental Section

General: All the enantiomeric amino acids were commercially available and used as received without further purification. The macrocyclic ligand TMeQ[6] was prepared according to literature methods.[1] Elemental analyses (C, H, and N) were performed on a PE 240C elemental analyzer.

Crystal structure Determination: X-ray data of complexes **1**-**7** were collected on a computer-controlled Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using ω and φ scan model at 273 or 293 K. Lorentz polarization and absorption corrections were applied. All structures were solved by direct methods with SHELXS-97, and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package.[2] Anisotropic displacement parameters were assigned to all non-hydrogen atoms. The carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. For the complexes **5**, **6** and **7**, the SQUEEZE option in PLATON program was applied to remove the nitrate and chloride anions, and solvent waters because they could not be satisfactorily modeled.[3] In order to obtain regular displacement parameters, some lattice water molecules in complexes **5** and **6** were given partial occupancy factors. A summary of crystal data, intensity measurements, structure solution, and refinement for all the seven complexes are given in Table 1. The Flack parameters of the complexes **1**-**7** indicate that their absolute configurations are correct. CCDC 1525001 - 1525007 contain the supplementary crystallographic data for complexes **1**-**7**.

Preparation of complexes:

{D-Gln@TMeQ[6]}·Cl·11H_2O (1) and {L-Gln@TMeQ[6]}·Cl·11H_2O (2): TMeQ[6]·10H_2O (12.3 mg, 0.01 mmol) and D-Gln (13.84mg, 0.095mmol) were dissolved in 5.0 mL solution of 1.0 mol·L^{-1} hydrochloric acid. The mixture was heated at 60 °C for *ca.* 10 min and then left in an open beaker. About five days later colorless crystals of complex **1** were obtained in 35% yield (based on TMeQ[6]). Anal. Calcd for $C_{45}H_{77}N_{26}O_{26}Cl$ (**1**): C, 37.70; H, 5.41; N, 25.40. Found: C, 37.75; H, 5.51; N, 25.47. Complex (**2**) was obtained as the method of **1** and the D-Gln is replaced by L-Gln. 35% yield based on TMeQ[6]. Anal. Calcd for $C_{45}H_{77}N_{26}O_{26}Cl$ (**2**): C, 37.70; H, 5.41; N, 25.40. Found: C, 37.78; H, 5.49; N, 25.47.

{Cd(H_2O)$_5$(D-Met)@TMeQ[6]}·(NO_3)$_2$·10H_2O (3): $Cd(NO_3)_2·4H_2O$ (17.8mg, 0.057mmol) and TMeQ[6]10H_2O (12.3 mg, 0.01 mmol) were added to an aqueous solution (5.0 ml) of D-Met (28.26 mg, 0.19 mmol). The mixture was stirred and heated at 50 ^oC for 10 min and then filtered. Slow evaporation of the filtrate solution over a period of 1 weeks provided colorless crystals. Yield: 0.0063 g (40% based on TMeQ[6]). Anal. Calcd for $C_{45}H_{84}N_{27}O_{35}CdS$ (**3**): C, 31.65; H, 4.96; N, 22.14. Found: C, 31.61; H, 5.01; N, 22.10.

{Cd(H_2O)$_5$(L-Met)@TMeQ[6]}·(NO_3)$_2$·10H_2O (4), D-Ser∩TMeQ[6]·Cl·10H_2O (5), L-Ser∩TMeQ[6]·Cl·10H_2O (6) and {TMeQ[6]∩Cd(H_2O)$_3$D-Val∩TMeQ[6]}·(NO_3)$_2$·21H_2O (7): All these complexes were obtained following the method described above for **3**. The yields based on TMeQ[6] for these complexes are in the range 30-40%. Anal. Calcd for $C_{45}H_{84}N_{27}O_{35}CdS$ (**4**): C, 31.65; H, 4.96; N, 22.14. Found: C, 31.60; H, 5.02; N, 22.11. Anal. Calcd for $C_{43}H_{72}N_{25}O_{25}Cl$ (**5**): C, 37.57; H, 5.28; N, 25.47. Found: C, 35.53; H, 5.26; N, 25.57. Anal. Calcd for $C_{43}H_{72}N_{25}O_{25}Cl$ (**6**): C, 37.57; H, 5.28; N, 25.47. Found: C, 37.72;

H, 5.35; N, 25.55. Anal. Calcd for $C_{85}H_{139}N_{51}O_{53}Cd$ (**7**): C, 36.00; H, 4.94; N, 25.19. Found: C, 35.93; H, 5.00; N, 25.17.

Table 1. Crystal data as well as details of data collection and refinement for complexes **1**-**7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{45}H_{77}N_{26}O_{26}Cl$	$C_{45}H_{77}N_{26}O_{26}Cl$	$C_{45}H_{84}N_{27}O_{35}CdS$	$C_{45}H_{84}N_{27}O_{35}CdS$	$C_{43}H_{72}N_{25}O_{25}Cl$	$C_{43}H_{72}N_{25}O_{25}Cl$	$C_{85}H_{139}N_{51}O_{53}Cd$
M_r	1433.78	1433.78	1707.85	1707.85	1374.71	1374.71	2835.87
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$P1$	$P1$	$P2_1$	$P2_1$	$P2_1$
a (Å)	13.3102(19)	13.2985(15)	11.9992(9)	12.0385(11)	13.219(3)	13.277(2)	13.4651(9)
b (Å)	17.025(2)	17.0458(19)	12.9523(5)	12.9653(6)	17.089(4)	17.119(3)	16.3400(11)
c (Å)	14.896(2)	14.9506(17)	12.9670(5)	12.9988(6)	15.467(3)	15.609(3)	29.934(2)
α (deg)	90	90	117.1840(10)	117.301(2)	90	90	90
β (deg)	108.860(4)	108.985(3)	105.147(2)	93.649(2)	112.608(7)	112.981(2)	100.665(2)
γ (deg)	90	90	93.662(2)	105.198(2)	90	90	90
V (Å^3)	3194.4(8)	3204.7(6)	1690.55(16)	1699.36(19)	3225.5(12)	3266.4(10)	6472.3(8)
Z	2	2	1	1	2	2	2
Dc (g·cm^{-3})	1.491	1.486	1.678	1.669	1.415	1.398	1.455
μ (mm^{-1})	0.163	0.162	0.470	0.468	0.156	0.154	0.277
F(000)	1508	1508	887	887	1444	1444	2956
Data/params	6211/885	11355/885	9509/982	6445/974	6494/849	6127/858	21388/1621
θ (deg)	1.44-26.00	1.44-26.00	1.80-25.00	1.79-26.00	1.43-26.00	1.42-25.99	0.69-25.10
GOF(F^2)	1.003	1.015	1.003	1.003	1.013	1.013	1.013
R_1[$I>2(I)$]	0.0989	0.0963	0.0456	0.0853	0.0776	0.0667	0.0438

wR_2(all data)	0.3059	0.2852	0.1284	0.2464	0.2288	0.1873	0.1132
Flack parameter	0.00(9)	0.0(3)	0.014(16)	0.00(16)	0.00(17)	0.00(7)	0.026(13)
CCDC number	1525001	1525002	1525003	1525004	1525005	1525006	1525007

Table 2. Selected bond lengths (Å) for complexes **3** and **7**.

3	O(1W)-Cd(1)	2.270(3)	**7**	O(1W)-Cd(1)	2.259(2)
	O(2W)-Cd(1)	2.232(4)		O(2W)-Cd(1)	2.313(3)
	O(3W)-Cd(1)	2.261(4)		O(3W)-Cd(1)	2.348(2)
	O(4W)-Cd(1)	2.312(3)		O(14)-Cd(1)	2.622(2)
	O(5W)-Cd(1)	2.334(3)		O(17)-Cd(1)	2.3506(19)
	O(13)-Cd(1)	2.215(3)		O(21)-Cd(1)	2.367(2)
				O(26)-Cd(1)	2.2996(17)

Notes and references

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