Supporting Information for

Influence of lower rim *C*-methyl group on crystal forms and metal complexation of resorcinarene bis-crown-5

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Synthesis and characterization

C-methyl bis-crown-5 (**1**) was synthesized as previously reported resorcinarene bis-crowns[1] from *C*-methyl tetramethoxy resorcinarene[2] using Cs_2CO_3 or K_2CO_3 as a base. The product was purified twice with flash chromatography: with neutral alumina column using $CHCl_3$:acetone 9:1 as an eluent (R_f = 0.68), and with silica column using $CHCl_3$:acetone 8:2 as an eluent. Recrystallization from chloroform:methanol afforded white crystals with 17 % yield. mp 269—272 °C; (Found: C, 66.56; H, 7.37. $C_{52}H_{68}O_{14}\cdot H_2O$ requires C, 66.79; H, 7.54 %); δ_H(500 MHz, $CDCl_3$) 1.41—1.47 (m, 12H; C*H*$_3$), 3.26—3.40 (m, 8H; OC*H*$_2$), 3.43—3.50 and 3.45 (overlapping m and s, 8H; OC*H*$_2$ and OC*H*$_3$), 3.52—3.61 (m, 4H; OC*H*$_2$), 3.61—3.71 (m, 4H; OC*H*$_2$), 3.74—3.82 (m, 6H; OC*H*$_2$), 3.89—4.00 and 3.93 (overlapping m and s, 10H; OC*H*$_2$ and OC*H*$_3$), 4.28 (t, ^3J (H,H) = 4.1, 1H; OC*H*$_2$), 4.30 (t, ^3J (H,H) = 4.1, 1H; OC*H*$_2$), 4.51—4.60 and 4.56 (overlapping m and t, ^3J (H,H) = 7.6, 6H; ArC*H* and OC*H*$_2$), 5.86 (s, 2H; Ar*H*), 6.10 (s, 2H; Ar*H*), 6.74 (s, 2H; Ar*H*), 7.24 (s, 2H; Ar*H*) ppm; δ_C(126 MHz, $CDCl_3$) 19.67 (*C*H$_3$), 20.27 (*C*H$_3$), 31.02 (Ar*C*H), 31.08 (Ar*C*H), 55.77 (O*C*H$_3$), 56.03 (O*C*H$_3$), 68.78 (O*C*H$_2$), 69.58 (O*C*H$_2$), 70.22 (O*C*H$_2$), 70.85 (O*C*H$_2$), 70.94 (O*C*H$_2$), 71.06 (O*C*H$_2$), 71.62 (O*C*H$_2$), 71.80 (O*C*H$_2$), 97.63 (*Ar*H), 97.72 (*Ar*H), 125.02 (*Ar*), 125.21 (*Ar*H), 125.62 (*Ar*), 126.31 (*Ar*H), 129.27 (*Ar*), 129.78 (*Ar*), 154.35 (*Ar*O), 155.05 (*Ar*O), 155.68 (*Ar*O), 156.07 (*Ar*O) ppm; *m/z* (ESI-TOF) 939 (M + Na^+, 100%); 955 (M + K^+, 93).

C-methyl mono-crown-5 (**2**) was obtained as a side product when K_2CO_3 was used as a base. The product was separated from **1** using flash chromatography with neutral alumina column and $CHCl_3$:acetone 9:1 as an eluent (R_f = 0.12). The product was purified with silica column using $CHCl_3$:acetone 8:2 as an eluent and crystallized from $CHCl_3$ yielding off-white crystals (3.6 % yield). mp 241.0—243.5 °C; (Found: C, 64.57; H, 6.79. $C_{44}H_{54}O_{11}\cdot 0.5CHCl_3\cdot 0.5H_2O$ requires C, 64.58; H, 55.94 %); δ_H(500 MHz, $(CD_3)_2CO$) 1.32—1.47 (m, four overlapping d, 12H; CH3), 3.18—3.23 (m, 1H; OC*H*$_2$), 3.27—3.31 (m, 2H; OC*H*$_2$), 3.33—3.43 and 3.39 (overlapping m and s, 5H; OC*H*$_2$ and OC*H*$_3$), 3.46 (s, 3H; OC*H*$_3$), 3.49—3.53 (m, 2H; OC*H*$_2$), 3.55—3.64 (m, 2H; OC*H*$_2$), 3.67—3.78 (m, 2H; OC*H*$_2$), 3.78—3.85 and 3.83 (overlapping m and s, 4H; OC*H*$_2$ and OC*H*$_3$) 3.86—3.98 (overlapping m and s, 5H; OC*H*$_2$ and OC*H*$_3$), 4.23—4.29 (m, 1H; OC*H*$_2$), 4.48 (q, ^3J (H,H) = 7.2, 1H; ArC*H*), 4.53—4.61 (m, 4H; ArC*H* and OC*H*$_2$), 5.92 (s, 1H; Ar*H*), 5.97 (s, 1H; Ar*H*), 6.20 (s, 1H; Ar*H*), 6.29 (s, 1H; Ar*H*), 6.52 (s, 1H; Ar*H*), 6.59 (s, 1H; O*H*), 6.86 (s, 1H; Ar*H*), 7.13 (s, 1H; Ar*H*), 7.21 (s, 1H; Ar*H*), 7.93 (s, 1H; O*H*) ppm; δ_C(126 MHz, $(CD_3)_2CO$) 19.73 (*C*H$_3$), 19.94 (*C*H$_3$), 20.44 (*C*H$_3$), 20.86 (*C*H$_3$), 31.38 (Ar*C*H), 31.47 (Ar*C*H), 31.69 (Ar*C*H), 31.81 (Ar*C*H), 55.82 (O*C*H$_3$), 55.97 (O*C*H$_3$), 56.06 (O*C*H$_3$), 56.79 (O*C*H$_3$), 69.47 (O*C*H$_2$), 70.07 (O*C*H$_2$), 70.83 (O*C*H$_2$), 71.22 (O*C*H$_2$), 71.59 (O*C*H$_2$), 71.81 (O*C*H$_2$), 72.11 (O*C*H$_2$), 72.15 (O*C*H$_2$), 99.09 (*Ar*H), 99.38 (*Ar*H), 100.09 (*Ar*H), 100.40 (*Ar*H), 122.67 (*Ar*), 124.38 (*Ar*), 125.42 (*Ar*H), 125.90 (*Ar*H + *Ar*), 126.24 (*Ar*H), 126.41 (*Ar*H), 126.48 (*Ar*), 126.88 (*Ar*), 127.65 (*Ar*), 130.21 (*Ar*), 130.47 (*Ar*), 153.77 (*Ar*O), 154.21 (*Ar*O), 155.23 (*Ar*O), 155.94 (*Ar*O), 156.03 (*Ar*O), 156.91 (*Ar*O), 157.01 (*Ar*O), 157.56 (*Ar*O) ppm; m/z (ESI-TOF) 781 (M + Na^+, 100%); 797 (M + K^+, 46).

Cavity diameter

The cavity diameter is calculated from average O···O distances as shown below.

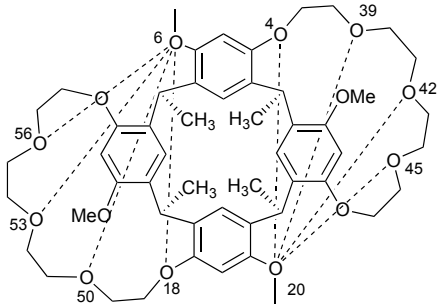

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Table 1. Cavity O···O distances for bis-crown **1** (Å).

	1-I	**1**-II	**1**-III	**1**-IV	**1**-V	**1**-Cs2	**1**-Ag2	**1**-Ag1
O20···O4	4.6056(1)	4.431(3)	4.580(2)	4.395(3)	4.297(5)	5.877(4)	4.705(5)[1]	4.570(5)
O20···O39	5.1505(1)	5.499(3)	4.421(3)	4.143(4)	3.985(4)	6.387(4)	4.129(5)[1]	4.427(6)
O20···O42	4.6373(1)	5.646(3)	5.064(3)	5.186(4)	4.745(4)	5.665(4)	3.284(5)[1]	5.619(5)
O20···O45	4.7116(1)	5.255(3)	5.874(2)	6.135(4)	5.252(5)	3.792(4)	5.122(5)[1]	5.740(5)
O6···O18	4.8040(1)	4.674(3)	4.552(2)	4.325(4)	4.403(5)	5.805(4)	[2]	4.468(6)
O6···O50	6.1459(1)	5.417(3)	5.176(2)	4.685(5)	3.954(5)	6.326(4)	[2]	5.140(7)
O6···O53	5.1433(1)	4.985(3)	5.070(2)	4.340(5)	4.706(5)	5.567(5)	[2]	5.090(6)
O6···O56	4.5702(7)	4.770(3)	5.133(2)	5.071(4)	5.348(5)	3.636(7)	[2]	4.753(8)

[1] O20 corresponds O6 (2-X,+Y,3/2-Z). [2] The second cavity is identical due to symmetry.

Table 2. Cavity O···O distances for mono-crown **2** (Å).

	2-I	**2**-II
O20···O4	5.066(3)	4.4923(15)
O20···O39	4.380(3)	4.1288(17)
O20···O42	4.402(4)	5.4757(16)
O20···O45	5.612(4)	4.8211(17)
O68···O56[1]	5.121(3)	
O68···O89[1]	4.579(3)	
O68···O92[1]	4.433(3)	
O68···O95[1]	5.091(4)	

[1] The second molecule in the asymmetric unit.

Crystallographic tables

Table 3. Metal coordination bond lengths.

1-Cs2	(Å)	**1**-Ag2	(Å)	**1**-Ag1	(Å)
Cs2···F2	3.473(4)	Ag1···O6[1]	2.536(3)	Ag1···O39	2.427(4)
Cs2···F5	3.409(4)	Ag1···39	2.362(4)	Ag1···O42	2.439(4)
Cs2···F6	3.111(3)	Ag1···O42	2.507(3)	Ag1···O206	2.312(5)
Cs2···O6	3.223(3)	Ag1···C10	2.634(5)	Ag1···C11	2.606(5)
Cs2···O18	3.206(3)	Ag1···C9	2.480(4)	Ag1···C12	2.497(5)
Cs2···O50	3.106(3)				
Cs2···O53	3.085(3)				
Cs2···O56	3.130(5)				
Cs2···C22	3.585(3)				
Cs2···C23	3.554(3)				
Cs2···C24	3.607(3)				
Cs2···C27	3.600(4)				
Cs1···F1[2]	3.253(3)				
Cs1···F2	3.492(4)				
Cs1···F3	3.395(4)				
Cs1···F4	3.264(3)				
Cs1···O4	3.309(3)				
Cs1···O20	3.252(3)				
Cs1···O39	3.138(3)				
Cs1···O42	3.149(3)				
Cs1···O45	3.226(3)				
Cs1···C12	3.676(4)				
Cs1···C13	3.680(4)				

[1]2-X,+Y,3/2-Z; [2]-X,1-Y,1-Z

Table 4. Hydrogen bonds in **1**-I (D···A < 3.5 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
C30	H30A	O25[1]	0.96	2.54	3.450(2)	158.6
C36	H36A	O39[2]	0.96	2.77	3.476(3)	130.5
C40	H40B	O27[3]	0.97	2.71	3.492(2)	138.6
C46	H46B	O42	0.97	2.48	3.152(2)	126.4
C49	H49A	O53	0.97	2.45	3.121(2)	125.9
C51	H51A	O18	0.97	2.66	3.268(2)	121.1
C51	H51B	O13[2]	0.97	2.48	3.362(2)	150.9

[1]1+X,+Y,+Z; [2]+X,1/2-Y,-1/2+Z; [3]+X,1/2-Y,1/2+Z

Table 5. Hydrogen bonds in **1**-II (D···A < 3.5 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
C33	H33C	O39[1]	0.98	2.76	3.468(3)	129.9
C36	H36C	O56[2]	0.98	2.65	3.382(4)	131.4
C40	H40C	O4	0.99	2.59	3.228(3)	122.2
C43	H43A	O45[3]	0.99	2.54	3.280(4)	131.6
C46	H46B	O42	0.99	2.51	3.123(4)	120.1
C47	H47A	O20	0.99	2.61	3.499(4)	149.0
C54	H54B	O11[4]	0.99	2.78	3.446(3)	125.2
C57	H57B	O53	0.99	2.42	3.062(4)	122.3

[1]1-X,-Y,-Z; [2]-X,1-Y,1-Z; [3]1-X,-Y,-1-Z; [4]+X,+Y,1+Z

Table 6. Hydrogen bonds in **1**-III (D···A < 3.5 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
C12	H12	O45	0.95	2.40	3.038(3)	124.4
C31	H31A	O50[1]	0.98	2.56	3.414(3)	145.0
C36	H36B	O13[2]	0.98	2.54	3.375(3)	142.9
C34	H34B	O27[3]	0.98	2.55	3.410(3)	145.8
C37	H37A	O56[4]	0.99	2.71	3.436(3)	130.1
C43	H43A	O42[5]	0.99	2.57	3.484(5)	153.8
C44	H44C	O45[6]	0.99	2.59	3.427(4)	142.6
C57	H57B	O53	0.99	2.42	3.073(3)	122.8
C100	H10C	O50	0.98	2.45	3.420(4)	172.8

[1]1+X,+Y,+Z; [2]+X,-1+Y,+Z; [3]+X,1+Y,+Z; [4]1-X,1-Y,1-Z; [5]1-X,2-Y,-Z; [6]2-X,2-Y,-Z

Table 7. Hydrogen bonds in **1**-IV (D···A < 3.5 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
C102	H10C	O39	0.97	2.41	3.247(9)	143.8
C12	H12	O45	0.93	2.42	3.133(5)	133.0
C36	H36A	O18[1]	0.96	2.35	3.287(5)	164.3
C49	H49A	O53	0.97	2.50	3.112(7)	120.7
C55	H55B	O25	0.97	2.50	3.124(6)	121.9
O100	H100	O42	0.82	2.01	2.815(9)	167.9

[1]-X,1-Y,-Z

Table 8. Hydrogen bonds in **1**-V (D···A < 3.5 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
C31	H31A	Cl6	0.98	2.65	3.452(6)	138.9
C38	H38B	O45[1]	0.99	2.75	3.483(6)	131.3
C40	H40A	O20	0.99	2.78	3.438(6)	124.3
C41	H41A	O45	0.99	2.55	3.181(6)	121.5
C44	H44B	O53[2]	0.99	2.46	3.232(7)	134.0
C49	H49A	O56[3]	0.99	2.75	3.379(6)	121.9
C51	H51A	O6	0.99	2.84	3.459(7)	121.0
C52	H52A	O56	0.99	2.57	3.219(6)	122.7
C55	H55B	O42[4]	0.99	2.61	3.257(6)	122.8
C100	H100	O50[1]	1.00	2.10	3.064(7)	160.5
C101	H101	O39[5]	1.00	2.38	3.124(7)	130.7
C101	H101	O42[5]	1.00	2.32	3.206(8)	147.8

[1]+X,1/2-Y,1/2+Z; [2]-1+X,1/2-Y,-1/2+Z; [3]+X,1/2-Y,-1/2+Z; [4]1+X,1/2-Y,1/2+Z; [5]-X,1/2+Y,1/2-Z

Table 9. Hydrogen bonds in **1**-Cs2 (D···A < 3.2 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
C35	H35A	F1[1]	0.98	2.67	3.177(5)	112.7
C36	H36A	F9[2]	0.98	2.46	3.086(5)	121.6

[1]-X,1-Y,1-Z; [2]+X,+Y,1+Z

Table 10. Hydrogen bonds in **1**-Ag2 (D···A < 3.2 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
C34	H34C	F5[1]	0.98	2.49	3.196(11)	128.5
C38	H38B	O45[2]	0.99	2.38	3.049(7)	124.3

[1]-1/2+X,-1/2+Y,+Z; [2]+X,1-Y,-1/2+Z

Table 11. Hydrogen bonds in **1**-Ag1 (D···A < 3.2 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
O206	H20A	O108[1]	0.93	1.79	2.49(3)	129.1
O206	H20B	O56[1]	0.93	2.16	2.994(9)	147.9
C5	H5	F103[2]	0.95	2.08	2.970(17)	156.3
C12	H12	O45	0.95	2.30	2.986(6)	128.9
C57	H57B	O53	0.99	2.40	3.125(10)	129.2
O200	H200	O203	0.85(2)	1.83(4)	2.68(2)	174(25)
O205	H20H	O107[3]	0.84(2)	1.97(10)	2.77(2)	161(29)
O205	H20I	O204	0.84(2)	1.80(5)	2.64(3)	173(32)

[1]+X,+Y,-1+Z; [2]1-X,1/2+Y,1-Z; [3]1/2-X,1-Y,-1/2+Z

Table 12. Hydrogen bonds in **2**-I (D···A < 3.5 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
O18	H18	O39[1]	0.827(18)	2.140(19)	2.966(3)	175(3)
O25	H25	O105[2]	0.814(19)	1.95(2)	2.757(3)	170(4)
O63	H63	O104[3]	0.814(18)	1.937(19)	2.750(3)	175(4)
O70	H70	O89[4]	0.808(18)	2.08(2)	2.869(3)	167(3)
O70	H70	O92[4]	0.808(18)	2.80(3)	3.296(4)	122(3)
O104	H10A	O70[4]	0.830(18)	2.11(2)	2.925(3)	167(4)
O104	H10B	O54[4]	0.807(18)	2.36(3)	2.996(3)	136(3)
O105	H10C	O18	0.828(19)	2.14(2)	2.963(3)	171(4)
O105	H10D	O6	0.850(18)	2.42(3)	2.985(3)	125(3)
C1A	H1A	O89	1.00	2.67	3.458(19)	136.0
C12	H12	O45[5]	0.95	2.46	3.380(4)	163.8
C43	H43A	O105[1]	0.99	2.24	3.198(4)	162.1
C44	H44B	O11	0.99	2.55	3.203(4	123.3
C46	H46A	O61	0.99	2.60	3.332(4)	130.4
C47	H47A	O45[5]	0.99	2.37	3.343(5)	166.6
C86	H86B	O95[6]	0.98	2.56	3.464(4)	153.9
C93	H93B	O63[7]	0.99	2.45	3.248(4)	137.1
C96	H96B	O92	0.99	2.37	3.078(5)	127.5
C100	H100	O39[1]	1.00	2.61	3.414(5)	137.3
C100	H100	O42[1]	1.00	2.53	3.355(5)	139.1

[1]2-X,2-Y,2-Z; [2]1-X,1-Y,2-Z; [3]1+X,1+Y,+Z; [4]1-X,2-Y,1-Z; [5]2-X,3-Y,2-Z; [6]1-X,1-Y,1-Z; [7]-1+X,-1+Y,+Z

Table 13. Hydrogen bonds in **2**-II (D···A < 3.5 Å, D-H-A >120°)

D	H	A	D···H (Å)	H···A (Å)	D···A (Å)	D-H-A (°)
O25	H25	O42[1]	0.848(15)	1.837(15)	2.6832(16)	176(2)
O18	H18	O42	0.846(14)	2.057(15)	2.8856(16)	165.9(18)
C26	H26	O42[1]	0.95	2.65	3.330(2)	129.1
C37	H37B	O20	0.99	2.61	3.493(2)	148.3
C41	H41A	O25[2]	0.99	2.70	3.470(3)	135.2
C41	H41B	N104[3]	0.99	2.48	3.428(7)	159.9
C43	H43A	O25[2]	0.99	2.49	3.384(2)	150.7
C43	H43B	O39	0.99	2.61	3.232(3)	121.0
C102	H10A	O18[2]	0.98	2.46	3.208(17)	133.2
C105	H10E	O18[2]	0.98	2.81	3.445(17)	123.4

[1]-1+X,1/2-Y,-1/2+Z; [2]-X,1/2+Y,1/2-Z; [3]1-X,1-Y,1-Z

Table 14. Torsion angles for the crown bridges in bis-crown **1**.

	1-I	**1**-II	**1**-III	**1**-IV	**1**-V	**1**-Cs2	**1**-Ag2	**1**-Ag1
O4-C37-C38-O39	-69.4(2)	-72.6(3)	84.7(3)	-80.6(4)	88.1(5)	-72.7(4)	70.7(5)	74.0(5)
O39-C40-C41-O42	-69.8(2)	-59.0(4)	73.1(4)	-73.0(4)	68.2(5)	66.3(4)	-62.5(6)	64.5(7)
O42-C43-C44-O45	-75.9(2)	-67.2(4)	63.2(4)	-58.6(7)	79.7(6)	-67.9(5)	87.7(6)	-68.6(6)
O45-C46-C47-O11	176.0(1)	64.4(4)	78.8(3)	-80.7(4)	67.8(5)	-81.4(5)	-72.5(5)	72.8(6)
O18-C48-C49-O50	-73.9(2)	-71.7(3)	-72.4(3)	171.0(7)	88.3(5)	-68.2(4)	[1]	-72.0(11)
O50-C51-C52-O53	-76.5(2)	-73.5(3)	-76.5(3)	73.7(7)	68.2(5)	65.4(5)	[1]	52(2)
O53-C54-C55-O56	-73.6(2)	-65.2(3)	-68.2(3)	86.0(4)	82.9(6)	-63.0(12)	[1]	59.7(16)
O56-C57-C58-O25	93.9(2)	-173.8(2)	-177.9(2)	-84.0(4)	72.1(5)	-84.8(9)	[1]	-163.3(6)

[1] The second crown bridge is identical due to symmetry.

Table 15. Torsion angles for the crown bridge in mono-crown **2**.

	2-I	**2**-II
O4-C37-C38-O39	-86.2(3)	-176.03(13)
O39-C40-C41-O42	-81.7(4)	-73.5(2)
O42-C43-C44-O45	74.1(4)	66.8(2)
O45-C46-C47-O11	-78.9(3)	179.77(14)
O56-C87-C88-O89[1]	69.7(4)	
O89-C90-C91-O92[1]	-63.0(4)	
O92-C93-C94-O95[1]	-79.3(4)	
O95-C96-C97-O77[1]	174.5(3)	

[1] The second molecule in the asymmetric unit.

References

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