Supplementary material

Complexation of biologically essential (mono- and divalent) metal cations to cucurbiturils: A DFT/SMD evaluation of the key factors governing the host-guest recognition

Nikoleta Kircheva,[a] Stefan Dobrev,[a] Lyubima Dasheva,[b] Iskra Koleva,[b]
Valya Nikolova,[b] Silvia Angelova [a*] and Todor Dudev[b*]

[a] *Institute of Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
[b] *Faculty of Chemistry and Pharmacy, Sofia University "St. Kl. Ohridski", 1164 Sofia, Bulgaria*

Table S1. BSSE-corrected Gibbs energies for the complex formation in the gas phase (superscript 1), and in a water environment (superscript 78), for the CB[n], n=5-8, complex formation with bare Mg^{2+} cations, in kcal mol^{-1}.

Reaction	ΔG^{1}	ΔG^{78}
M062X/6-31G(d,p)		
CB[5] + Mg^{2+}→ CB[5]-Mg^{2+}	-322.5	-56.7
CB[6] + Mg^{2+}→ CB[6]-Mg^{2+}	-299.0	-48.4
CB[7] + Mg^{2+}→ CB[7]-Mg^{2+}	-291.1	-42.5
CB[8] + Mg^{2+}→ CB[8]-Mg^{2+}	-285.8	-40.2

Table S2. BSSE-corrected Gibbs energies for the complex formation in the gas phase (superscript 1), and in a water environment (superscript 78), for the $CB[7]^{m+}$ (M = Na, K, Mg, Ca; m = 1,2) complex formation, in kcal mol^{-1}.

Reaction	ΔG^{1}	ΔG^{78}
M062X/6-31G(d,p)		
CB[7] + Na^{+}→ CB[7]-Na^{+}	-77.7	-21.9
CB[7] + K^{+}→ CB[7]-K^{+}	-63.3	-16.4
CB[7] + Mg^{2+}→ CB[7]-Mg^{2+}	-291.1	-42.5
CB[7] + Ca^{2+}→ CB[7]-Ca^{2+}	-219.1	6.4

Table S3. BSSE-corrected Gibbs energies for the complex formation in the gas phase (superscript 1), and in a water environment (superscript 78), for the CB[7]-2Mg^{4+} complex formation in different positions of the second Mg^{2+} , in kcal mol^{-1}.

Reaction	ΔG^{1}	ΔG^{78}
M062X/6-31G(d,p)		
CB[7] + Mg^{2+}→ CB[7]-Mg^{2+}	-291.1	-42.5
CB[7]-Mg^{2+} + Mg^{2+}→ CB[7]-2*Mg^{4+} (1;2)	-123.9	-37.3
CB[7]-Mg^{2+} + Mg^{2+}→ CB[7]-2*Mg^{4+} (1;3)	-68.5	-36.4
CB[7]-Mg^{2+} + Mg^{2+}→ CB[7]-2*Mg^{4+} (1;4)	-131.4	-45.7

Table S4. BSSE-corrected Gibbs energies for the complex formation in the gas phase (superscript 1), and in a water environment (superscript 78), for the CB[7]-$Na(H_2O)_6^{+}$, CB[7]-$K(H_2O)_6^{+}$, CB[7]-$Mg(H_2O)_6^{2+}$, CB[7]-$Ca(H_2O)_8^{+}$ and CB[7]-2*$Mg(H_2O)_6^{4+}$ complexes, in kcal mol^{-1}.

Reaction	ΔG^{1}	ΔG^{78}
M062X/6-31G(d,p)		
CB[7] + $Na(H_2O)_6^{+}$→ CB[7]-$Na(H_2O)_6^{+}$	-58.9	-22.2
CB[7] + $K(H_2O)_6^{+}$→ CB[7]-$K(H_2O)_6^{+}$	-46.7	-13.5
CB[7] + $Mg(H_2O)_6^{2+}$→ CB[7]-$Mg(H_2O)_6^{2+}$	-135.5	-28.0
CB[7] + $Ca(H_2O)_8^{2+}$→ CB[7]-$Ca(H_2O)_8^{2+}$	-121.1	-22.1
CB[7]-$Mg(H_2O)_6^{2+}$ + $Mg(H_2O)_6^{2+}$→ CB[7]-2*$Mg(H_2O)_6^{4+}$	20.4	-19.7

Table S5. Number of CB[n]O-Mg bonds and mean CB[n]O-Mg distances (Å).

Complex	M062X/6-31G(d,p)		B3LYP-D3/6-31G(d,p)	
CB[5]-Mg^{2+}	4	2.03	4	2.05
CB[6]-Mg^{2+}	3	1.94	3	1.94
CB[7]-Mg^{2+}	3	1.93	3	1.94
CB[8]-Mg^{2+}	3	1.93	3	1.94

Table S6. BSSE-corrected Gibbs energies for the complex formation in the gas phase (superscript 1), and in a water environment (superscript 78), for the CB[n], n=5-8, complex formation with bare Mg^{2+} cations, in kcal mol^{-1}.

Reaction	ΔG^{1}	ΔG^{78}	ΔG^{1}	ΔG^{78}
	M062X/6-31G(d,p)		**M062X/6-31+G(d,p)// M062X/6-31G(d,p)**	
CB[5] + Mg^{2+}→ CB[5]-Mg^{2+}	-322.5	-56.7	-315.6	-48.2
CB[6] + Mg^{2+}→ CB[6]-Mg^{2+}	-299.0	-48.4	-293.7	-41.7
CB[7] + Mg^{2+}→ CB[7]-Mg^{2+}	-291.1	-42.5	-285.8	-36.2
CB[8] + Mg^{2+}→ CB[8]-Mg^{2+}	-285.8	-40.2	-280.9	-33.9
	B3LYP-D3/6-31G(d,p)		**B3LYP-D3/6-31+G(d,p)// B3LYP-D3/6-31G(d,p)**	
CB[5] + Mg^{2+}→ CB[5]-Mg^{2+}	-327.5	-64.2	-317.4	-52.7
CB[6] + Mg^{2+}→ CB[6]-Mg^{2+}	-303.4	-53.2	-295.6	-44.4
CB[7] + Mg^{2+}→ CB[7]-Mg^{2+}	-296.6	-49.0	-288.8	-40.5

CB[8] + Mg^{2+}→ CB[8]-Mg^{2+}	-293.3	-47.0	-285.2	-38.5

Table S7. BSSE-corrected Gibbs energies calculated for the CB[5]-Mg^{2+} complex formation in the gas phase (superscript 1), and in a water environment (superscript 78) at different ambient conditions.

	M062X/6-31G(d,p)		**M062X/6-31+G(d,p)// M062X/6-31G(d,p)**	
Conditions	**ΔG^{1}**	**ΔG^{78}**	**ΔG^{1}**	**ΔG^{78}**
298.15 K; 1.0 atm	-322.5	-56.7	-315.6	-48.2
373.15 K; 1.0 atm	-320.5	-55.5	-313.7	-47.1
373.15 K; 10.0 atm	-318.8	-53.8	-312.1	-45.5

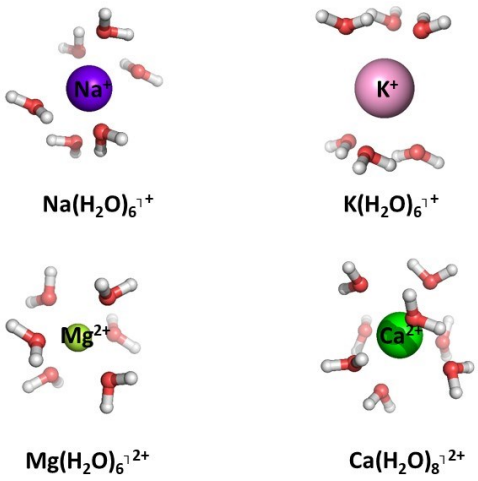

Figure S1. Optimized geometries of aqua ions of the studied mono- and divalent metals.