Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Complexation of trivalent metal cations (Al^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Lu^{3+}) to cucurbiturils: a DFT/SMD evaluation of the key factors governing the host–guest recognition

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Additional data

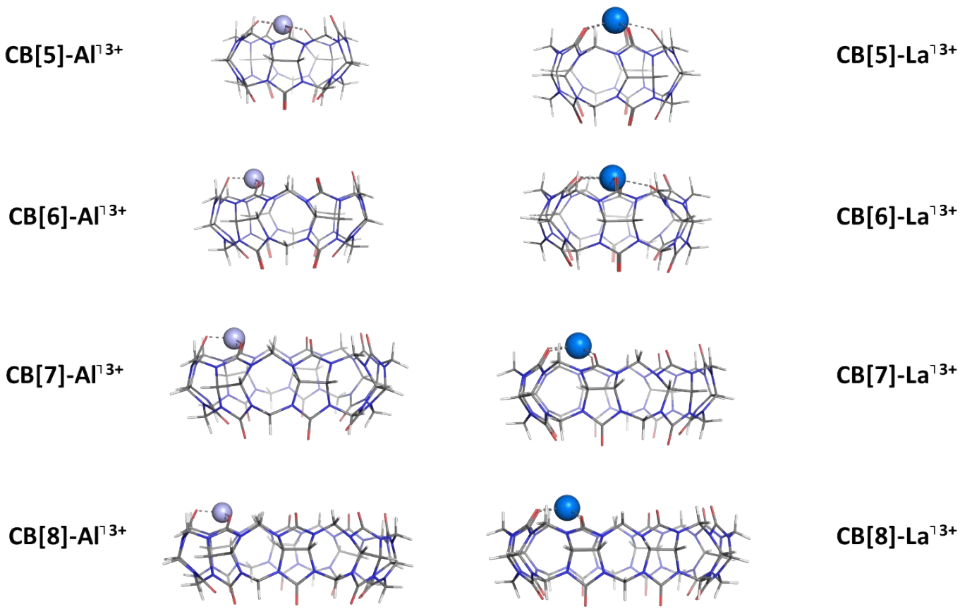

Figure S1. Optimized geometries of the CB[n], n = 5–8, complexes with bare Al^{3+} and La^{3+} cations (side view).

Table S1. CB[n]O-M distances and mean CB[n]O-M distances (Å).

CB[5]-Al^{3+}	CB[6]-Al^{3+}	CB[7]-Al^{3+}	CB[8]-Al^{3+}		CB[5]-La^{3+}	CB[6]-La^{3+}	CB[7]-La^{3+}	CB[8]-La^{3+}
1.819	1.718	1.720	1.719		2.409	2.532	2.352	2.363
1.856	1.756	1.756	1.755		2.403	2.438	2.356	2.358
1.857	1.718	1.720	1.718		2.406	2.606	2.357	2.358
1.820	1.73	1.73	1.73		2.409	2.458	2.352	2.363
1.84					2.406	2.506	2.35	2.36
					2.41	2.51		

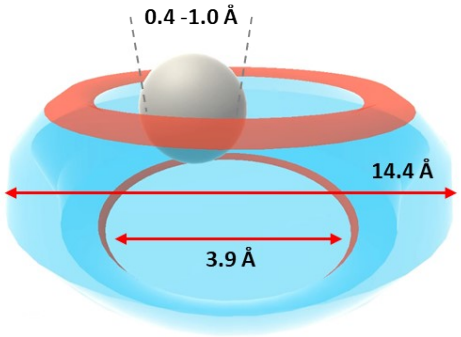

Figure S2. CB[6]/trivalent metal cations proportions. The relative ionic radii of Al^{3+}, Ga^{3+}, In^{3+}, La^{3+} and Lu^{3+} for cations in complexes with tetrahedral (Al, Ga and In) and octahedral (La and Lu) surroundings are listed in Table 3.

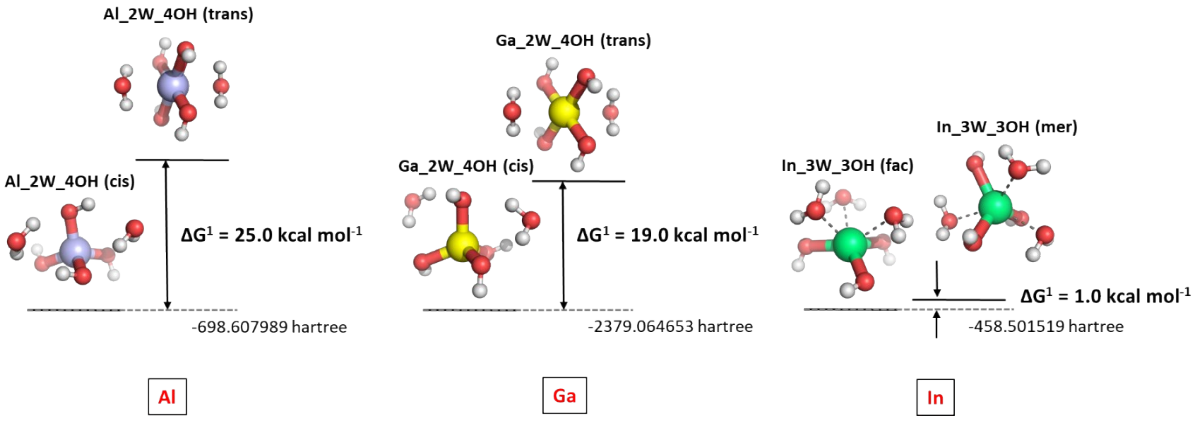

Figure S3. Optimized geometries of the hydrated metal cations Al^{3+}, Ga^{3+} and In^{3+} at neutral pH (pH≈7). The relative stability of the hydrated species in the gas phase, ΔG^1, is also given.

Table S2. Complex formation reactions between CB[6] and bare/hydrated M^{3+} cations, in kcal mol^{-1}.

Reaction	ΔG^{1}	ΔG^{78}
CB[6] + Al^{3+} → CB[6]-Al^{3+}	-723.0	-355.2
CB[6] + Ga^{3+} → CB[6]-Ga^{3+}	-727.7	-252.3
CB[6] + In^{3+} → CB[6]-In^{3+}	-529.7	-33.8
CB[6] + La^{3+} → CB[6]-La^{3+}	-449.2	59.0
CB[6] + Lu^{3+} → CB[6]-Lu^{3+}	-503.6	-2.5
CB[6] + $Al(H_2O)_6^{3+}$ → CB[6]-$Al(H_2O)_6^{3+}$	-257.8	-32.7
CB[6] + $Ga(H_2O)_6^{3+}$ → CB[6]-$Ga(H_2O)_6^{3+}$	-281.7	-33.7
CB[6] + $In(H_2O)_6^{3+}$ → CB[6]-$In(H_2O)_6^{3+}$	-217.4	-11.8
CB[6] + $La(H_2O)_8^{3+}$ → CB[6]-$La(H_2O)_8^{3+}$	-172.1	4.5
CB[6] + $La(H_2O)_9^{3+}$ → CB[6]-$La(H_2O)_9^{3+}$	-178.4	-11.7
CB[6] + $Lu(H_2O)_8^{3+}$ → CB[6]-$Lu(H_2O)_8^{3+}$	-187.7	-2.2
CB[6] + $Al(OH)_4(H_2O)_2^{-}$ → CB[6]-$Al(OH)_4(H_2O)_2^{-}$	-13.9	8.3
CB[6] + $Ga(OH)_4(H_2O)_2^{-}$ → CB[6]-$Ga(OH)_4(H_2O)_2^{-}$	-26.9	3.6
CB[6] + $In(OH)_3(H_2O)_3^{0}$ → CB[6]-$In(OH)_3(H_2O)_3^{0}$	-11.5	13.7

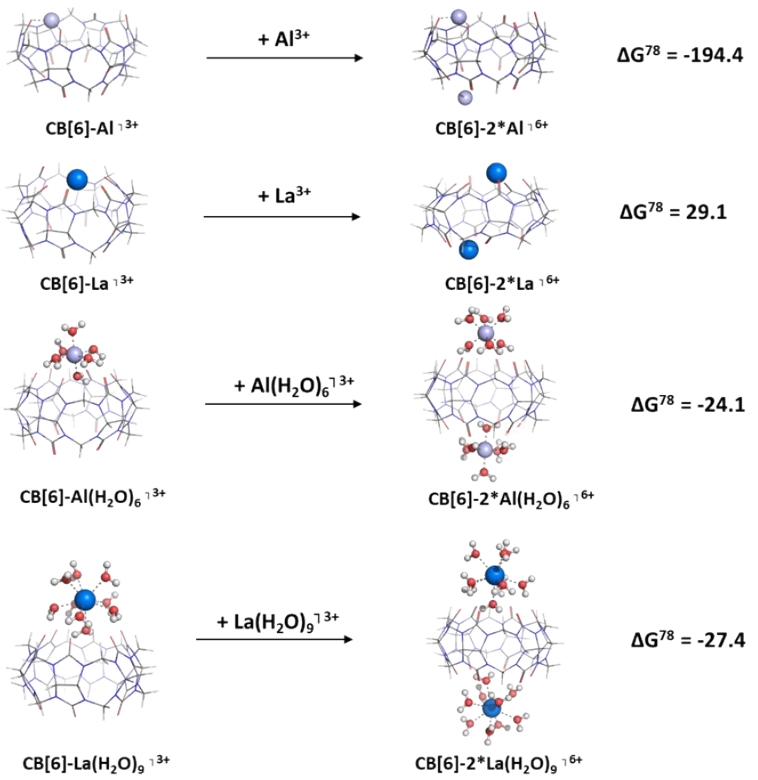

Figure S4. Optimized structures of complexes with 1:2 ligand-metal stoichiometry: CB[6]-2*Al, CB[6]-2*La, CB[6]-2*$Al(H_2O)_6$, CB[6]-2*$La(H_2O)_9$. The calculated Gibbs energies for complex formation in

water ΔG^{78} are in kcal mol^{-1}. The presence of second positively charged particle (M^{3+}) in the complex inflicts repulsive ion–ion interactions affecting both geometry and thermodynamics of the construct.

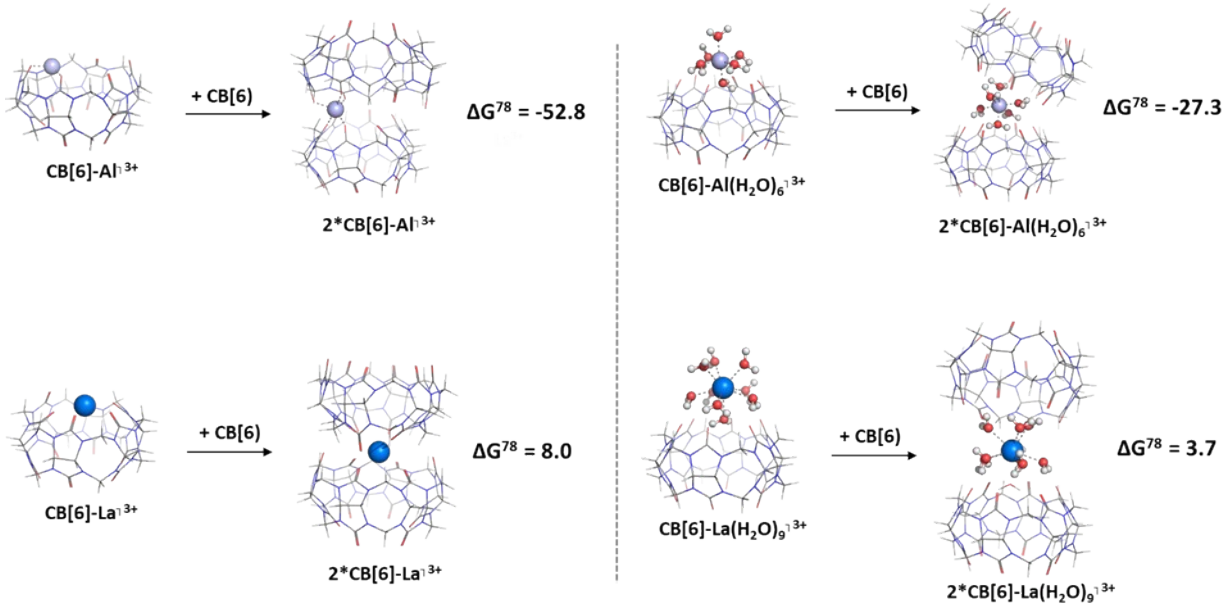

Figure S5. Optimized structures of complexes with 2:1 ligand-metal stoichiometry: 2*CB[6]-Al, 2*CB[6]-La, 2*CB[6]-Al$(H_2O)_6$ and 2*CB[6]-La$(H_2O)_9$. The calculated Gibbs energies for complex formation in water ΔG^{78} are in kcal mol^{-1}.