Factors Governing the Host-Guest Interactions between IIA/IIB Group Metal Cations and α-Cyclodextrin: a DFT/CDM Study

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Supplementary Information

Experimental structural data from Ca^{2+} - erythritol and Ca^{2+} - lactose complexes have been used to calibrate the theoretical method employed.

1) Ca^{2+}- erythritol complex

Erythritol ($C_4H_{10}O_4$), one of the simplest representatives of carbohydrates, was chosen as a model system to study the coordination behavior of hydroxyl groups to metal ions. A mean experimental distance of 2.410 Å was calculated from the experimental Ca-$O_{erythritol}$ distances (2.418 Å, 2.402 Å, 2.418 Å and 2.402 Å) of the X-ray structure, taken from Yang *et al.* (Figure S1):

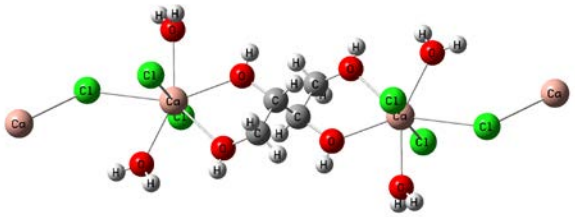

Figure S1.

In our model Ca^{2+} is coordinated to two hydroxyl groups from a single ligand molecule, two Cl^- ions and two water molecules (Figure S2):

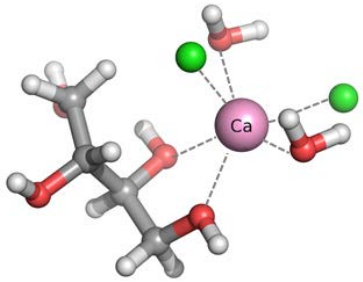

Figure S2.

Experimental and calculated mean Ca-O distances in Ca^{2+}-erythritol complexes, optimized at different levels of theory, are listed in Table S1.

Table S1. Experimental and calculated mean Ca^{2+}-$O_{erythritol}$ distances in Ca^{2+}-erythritol complex.

	Ca-$O_{erythritol}$ distance	Exp. – calc.
Exp. [S1]	2.410	
M062X/6-31G(d,p)	2.405	0.005
M062X/6-31+G(d,p)	2.413	-0.003
M062X/6-31+G(2d,p)	2.411	-0.001
M062X/6-311G(d,p)	2.374	0.036
M062X/6-311+G(d,p)	2.384	0.026
B3LYP/6-31G(d,p)	2.452	-0.042
B3LYP/6-31+G(d,p)	2.504	-0.094
B3LYP/6-31+G(2d,p)	2.470	-0.059
B3LYP/6-311G(d,p)	2.422	-0.012
B3LYP/6-311+G(d,p)	2.434	-0.024
HF/6-31G(d,p)	2.474	-0.064
HF/6-31+G(d,p)	2.500	-0.090
HF/6-31+G(2d,p)	2.492	-0.082
HF/6-311G(d,p)	2.470	-0.060
HF/6-311+G(d,p)	2.478	-0.068

2) Ca^{2+}- lactose complex

In the hydrated calcium bromide complex of lactose (4-O-β-D-galactopyranosyl-D-glucopyranose) the calcium ion binds to two lactose molecules and four water molecules. First lactose molecule is coordinated to the calcium ion through two oxygen atoms of its galactose moiety and the second one is coordinated through two oxygen atoms from its glucose moiety [S2]. In our model complex calcium ion binds to one galactose molecule, one glucose molecule and four water molecules (Figure S3). Thus, the calcium ion is surrounded by a similar shell, composed of eight oxygen atoms: four from water molecules and four from glucose/galactose hydroxyl groups. The M062X/6-31G(d,p) calculated Ca-$O_{lactose}$ mean distance, 2.506 Å, is very close to the experimental one of 2.500 Å.

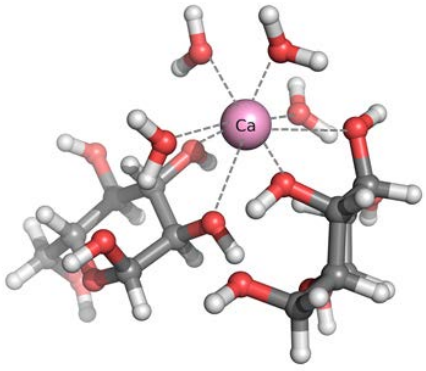

Figure S3.

Table S2. Thermodynamic parameters (in kcal/mol) in the gas-phase (superscript 1) and water environment (superscript 78) calculated for the metal complex formation reaction, αCD + $M^{2+} \rightarrow [\alpha CD\text{-}M]^{2+}$.

metal cation	Full optimization					Partial optimization (metal frozen)		Partial optimization (αCD frozen)	
	ΔE_{el}^{1}	ΔH^{1}	$T\Delta S^{1}$	ΔG^{1}	ΔG^{78}	ΔE_{el}^{1}	ΔG^{1}	ΔE_{el}^{1}	ΔG^{1}
Be^{2+}	-446.9	-447.3	-12.5	-434.8	-119.6	-195.2	-182.7	-286.8	-274.7
Mg^{2+}	-306.0	-306.1	-12.3	-293.8	-32.9	-161.3	-149.0	-211.0	-198.8
Ca^{2+}	-226.0	-226.7	-9.7	-217.0	-9.4	-135.3	-125.6	-182.2	-173.2
Sr^{2+}	-183.8	-182.5	-12.2	-170.3	13.4	-109.7	-97.5	-156.6	-143.1
Ba^{2+}	-165.7	-165.0	-11.7	-153.3	22.8	-91.6	-79.9	-137.0	-124.5
Zn^{2+}	-353.3	-353.4	-12.7	-340.8	-44.8	-183.0	-170.3	-237.9	-225.4
Cd^{2+}	-277.4	-277.9	-11.4	-266.6	13.0	-164.1	-152.7	-204.4	-193.5
Hg^{2+}	-284.7	-286.0	-10.9	-275.1	33.6	-184.2	-173.3	-217.8	-208.2

References

[S1] Yang, L.; Su, Y.; Xu, Y.; Wang, Z.; Guo, Z.; Weng, S.; Yan, C.; Zhang, S.; Wu, J. Interactions between Metal Ions and Carbohydrates. Coordination Behavior of Neutral Erythritol to Ca(II) and Lanthanide Ions, *Inorg. Chem*. **2003**, *42*, 5844−5856.

[S2] Bugg, C. E. Calcium Binding to Carbohydrates. Crystal Structure of a Hydrated Calcium Bromide Complex of Lactose, *J. Amer. Chem. Soc.*, **1973**, *95*, 908-913.