

Organomagnesium crown ethers and their binding affinities with Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , and Ca^{2+} ions - A theoretical study

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Abstract

Novel organomagnesium crown ether molecules have been computationally characterized for the first time using density functional theory (DFT). Monomer units of MgC_6 have been used as building blocks. The potential energy surface of the parent elemental composition, MgC_6H_2 , has been extensively explored using both DFT and coupled-cluster methods. It is concluded that the seven-membered ring isomer, 1-magnesacyclohept-4-en-2,6-diyne, is the thermodynamically most stable molecule at all levels. Thus, the latter has been used as the building block for organomagnesium crown ethers. Both alkali (Li^+ , Na^+ , and K^+) and alkaline-earth (Be^{2+} , Mg^{2+} , and Ca^{2+}) metal ions selective complexes have been theoretically identified. Binding energies (ΔE at 0 K) and thermally corrected Gibbs free energies (ΔG at 298.15 K) have been computed for these metal ions with MgC_6 -9-crown-3 and MgC_6 -12-crown-4 to gauge their binding affinities.

Keywords

organomagnesium crowns, host-guest molecules, alkali metal ions, alkaline earth metal ions, binding energies, Be^{2+} encapsulation

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INTRODUCTION

More than 10,000 crown ether molecules have been reported to date¹⁻⁵ since the original discovery of crown ethers accidentally happened in 1967 by Pedersen.^{6,7} However, the concept of crown ethers remains fascinating due to the potential applications of these molecules in various fields including (but not limited to) phase transfer catalysis,⁸ ion-sensing,⁹ nuclear waste management,¹⁰⁻¹² and analytical methods.¹³ The ability of crown ethers to recognize and trap different metal ions depending upon the size of the macrocyclic ring, type of the donor atom (N, O, and S and thus hard-soft interactions), and polarity of the medium strengthened their utility in various aspects.¹⁴⁻¹⁸

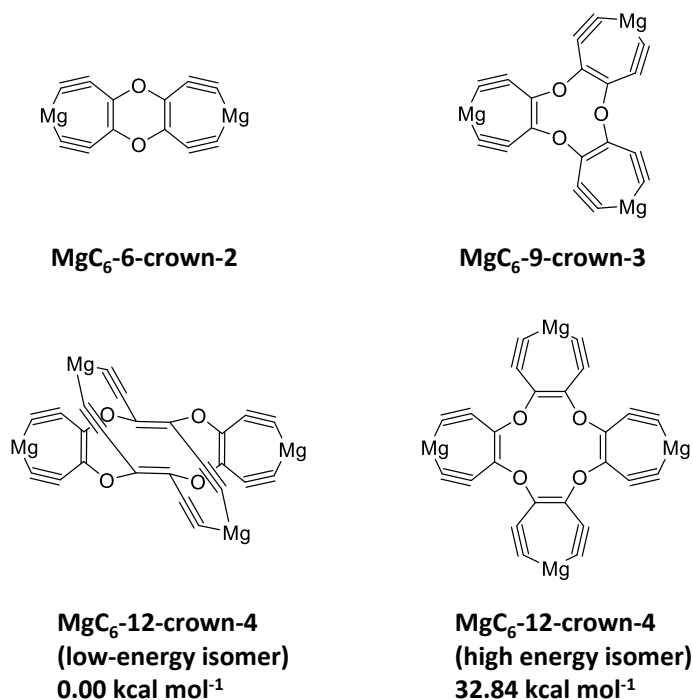


Figure 1: Organomagnesium crown ethers theoretically identified in this study. ZPVE-corrected relative energies are obtained at the B3LYP/6-311++G(2d,2p) level of theory.

Though toxic, beryllium and its alloys are indispensable for the aeronautic and space industry.^{19,20} This is due to their comparable mechanical properties to steel but at the same time non-magnetic and non-sparking. However, one of the major safety issues in using beryllium and its compounds is that it can cause the development of chronic beryllium disease.²¹⁻²³ For this reason, the beryllium chemistry is somewhat underdeveloped from an experimental perspective.²⁴ Nevertheless, designing ligands theoretically, which can effectively bind with Be²⁺ ion is an important study to consider. Here, we have computationally designed some novel organomagnesium crown ethers for the first time and studied their binding affinities computationally in the gas phase with both alkali (Li⁺, Na⁺, and K⁺) and alkaline-earth (Be²⁺, Mg²⁺, and Ca²⁺) metal ions. It is also noted here that separation of Li⁺ from Mg²⁺ ion remains as a challenge even to date.²⁵ Thus, designing ligands, which

could effectively bind one ion over the other is a key problem to address. Therefore, computational studies along these lines are well justified before explicitly starting the experimental works. In a previous theoretical study, the potential energy surface of MgC_6H_2 has been extensively explored by some of us using both DFT and coupled-cluster methods.²⁶ The thermodynamically most stable isomer for MgC_6H_2 was identified to be 1-magnesacyclohept-4-en-2,6-diyne. Thus, in this study, utilizing the cyclic MgC_6 as a base unit, we have computationally identified four different organomagnesium crown ether molecules, which are depicted in Figure 1. Optimized geometries of these molecules in the ball and stick model including energy differences in case of multiple structural isomers (MgC_6 -12-crown-4) are shown in Figure 2. The IUPAC names of MgC_6 -6-crown-2, MgC_6 -9-crown-3, and MgC_6 -12-crown-4 (two different isomers) are as follows: (i) MgC_6 -6C2 – 6,14-dimagnes-2,10-dioxatricyclo[9.5.0.0^{3,9}]hexadeca-1(11),3(9)-dien-4,7,12,15-tetrayne, (ii) MgC_6 -9C3 – 6,14,22-trimagnes-2,10,18-trioxatetracyclo[17.5.0.0^{3,9}.0^{11,17}]tetracosan-1(19),3(9),11(17)-trien-4,7,12,15,20,23-hexayne, (iii) MgC_6 -12C4 (low energy isomer) – 7,18,25,30-tetramagnes-3,11,14,22-tetraoxapentacyclo[11.9.5.5^{2,12}.0^{4,10}.0^{15,21}]dotriacontan-1,4(10),12,15(21)-tetraene-5,8,16,19,23,26,28,31-octayne, and (iv) MgC_6 -12C4 (high energy isomer) – 6,14,22,30-tetramagnes-2,10,18,26-tetraoxapentacyclo[25.5.0.0^{3,9}.0^{11,17}.0^{19,25}]dotriacontan-1(27),3(9),11(17),19(25)-tetraen-4,7,12,15,20,23,28,31-octayne. The IUPAC names derived here for these crown ether molecules have been cross checked with the OPSIN server.²⁷ At the moment, pentamers and hexamers have not been considered in this study due to the computational viability of performing the calculations and also the multiple number of structural isomers possible. Here, binding affinities with six different metal ions have been explicitly studied at five different level of theories each for MgC_6 -12C3 and MgC_6 -12C4. It is also noted here that solvent effects are not considered in this study as the current investigation predominantly focused on the intrinsic binding affinities within the gas-phase to thoroughly understand the molecular recognition of these new host molecules.

COMPUTATIONAL DETAILS

Geometry optimization and frequency calculations have been done using density functional theory (DFT) with the hybrid-functional B3LYP²⁸⁻³⁰ and the 6-311++G(2d,2p) basis set.^{31,32} All stationary points obtained at this level have been reoptimized including Grimme’s empirical dispersion corrections (D3)³³ with Becke-Johnson damping (D3BJ)^{34,35} to capture the geometrical changes due to dispersion (i.e., van der Waals) interactions.³⁶ Further, all geometries have been optimized with the TPSSh³⁷ hybrid-meta functional including D3BJ corrections. M06-2X³⁸ hybrid-meta functional had also been used. As the later already incorporates certain amount of dispersion correction within the functional itself, additional D3BJ corrections on top of this functional have not been done. All the organomagnesium crown ethers studied here are found to be stable (i.e., zero imaginary frequencies) at all these five different level of theories. All electronic structure calculations have been done with the Gaussian program package.³⁹

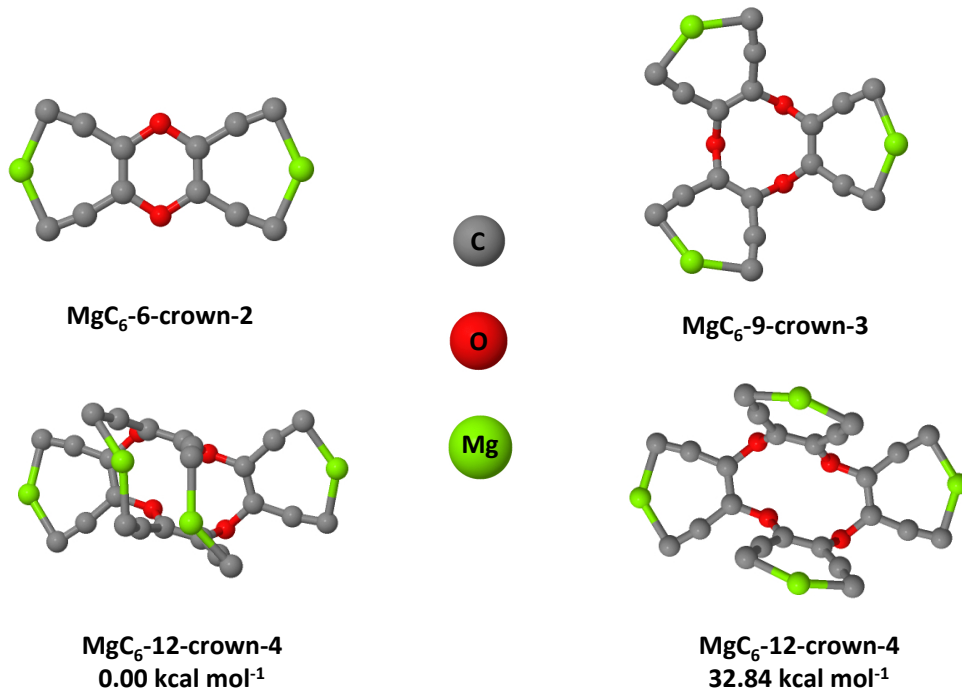


Figure 2: Optimized structures of organomagnesium crown ethers identified at the B3LYP/6-311++G(2d,2p) level of theory.

RESULTS AND DISCUSSION

The binding energies (ΔE at 0 K) and thermally corrected Gibbs free energies (ΔG at 298.15 K) computed for the metal ions with $\text{MgC}_6\text{-9C3}$ and $\text{MgC}_6\text{-12C4}$ at different level of theories have been collected in Table 1. They are calculated using the following equation

$$\Delta E = E_{\text{complex}} - (E_{\text{host}} + E_{\text{ion}}) \quad (1)$$

where, E_{complex} is the ZPVE-corrected value of the complex, E_{host} is the ZPVE-corrected value of the host, and E_{ion} is the energy of the ion. Similarly, Gibbs free energy values have been calculated using the corresponding thermally corrected energies. The key optimal parameters obtained at the M06-2X/6-311++G(2d,2p) level of theory are given in Table 2. For brevity, they are given only at one particular level.

$\text{M}^{+/2+}\text{-MgC}_6\text{-9C3}$

The binding energy values calculated for Li^+ are in the range of -63.42 to -68.34 (lowest to highest) kcal mol^{-1} . The values calculated by us at different levels closely matches with one of the trioxane derivatives reported elsewhere at the B3LYP/6-31++G(d,p) level.⁴⁰ Within group 2, the smallest ion, Be^{2+} exhibits the highest binding affinity at all levels. The ΔE values are in the range of -337.02 to -355.21 kcal mol^{-1} . The Gibbs free energy values (ΔG) are consistently 7 to 8 kcal mol^{-1} less than the binding energy values for all the six ions. The

ΔE values calculated for Li^+ , K^+ , and Be^{2+} are slightly higher compared with the ΔE values obtained by the low-energy higher homologue ($\text{MgC}_6\text{-12C4}$) at all levels. In general, binding affinity within a group (here group 1 and 2) decreases down the group. This periodic trend could be explained due to the increase in the ionic radii of the ions down a given group. Mg^{2+} ion makes covalent bonds with three oxygen atoms,⁴¹ and the chelated complex looks like a bowl. $\text{Mg}^{2+}\text{-O}$ bond length is 1.973 Å at the M06-2X/6-311++G(2d,2p) level of theory. The binding energies range from -211.71 to -225.17 kcal mol⁻¹.

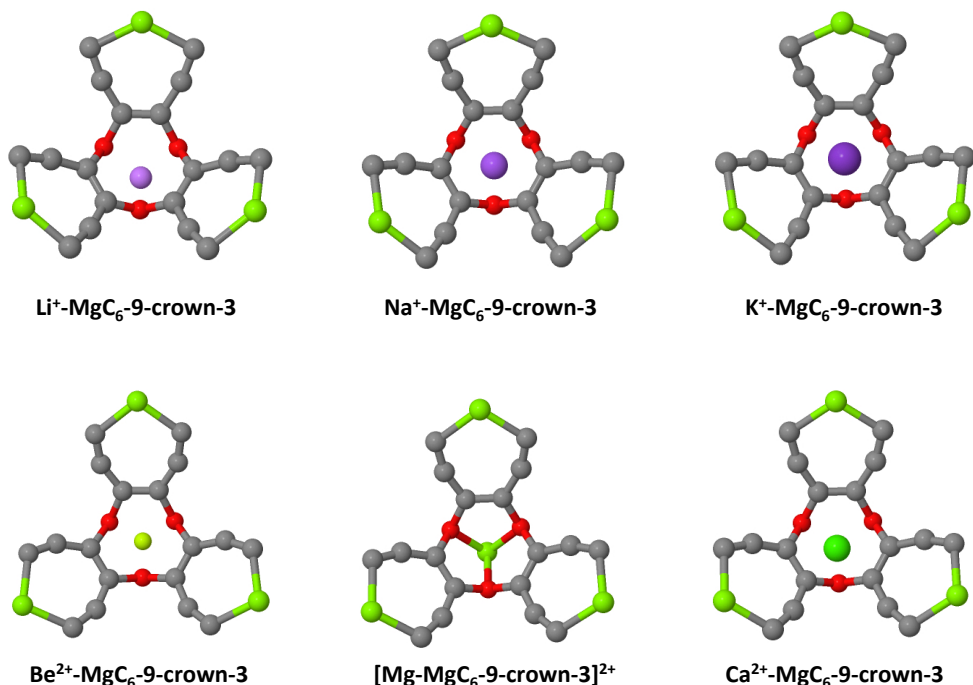


Figure 3: Optimized structures of metal-ion chelated organomagnesium crown ethers identified at the B3LYP/6-311++G(2d,2p) level of theory

$\text{M}^{+/2+}\text{-MgC}_6\text{-12C4}$

Unlike the lower homologue, $\text{MgC}_6\text{-9C3}$, for this system we found two isomers (see Figure 2). The most stable isomer forms a bridge between two MgC_6 units. The other isomer, which has no cross-link, is 32.84 kcal mol⁻¹ above the low-lying form at the B3LYP/6-311++G(2d,2p) level of theory. At the TPSSh/6-311++G(2d,2p) level of theory, the energy gap (ZPVE inclusive) between these two isomers is 37.95 kcal mol⁻¹. It is noted here that we could obtain the high energy form only at these two different levels (B3LYP and TPSSh). Calculations with Grimme's empirical dispersion corrections³³ involving D3BJ damping^{34,35} or the Truhlar's Minnesota functional, M06-2X,³⁸ that has certain amount of in-built empirical dispersion corrections consistently yield only the low-energy isomer upon optimization. Geometry optimization started with high-energy isomer always leads to the low-energy energy isomer with respect to these three different functionals (B3LYP-D3BJ,

TPSSH-D3BJ, and M06-2X) using the 6-311++G(2d,2p) basis set. Although complexes were found with both the isomers (see Figures 4 and 5) at all levels, we couldn't find the high-energy host isomer at these three different levels. Therefore, binding energies are not calculated at these levels (see Table 1).

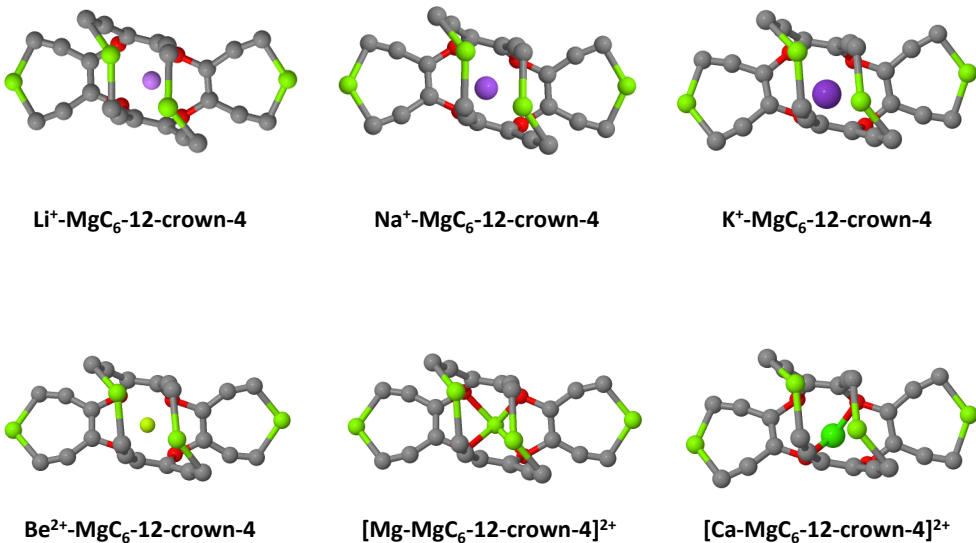


Figure 4: Optimized structures of metal-ion chelated MgC₆-12-crown-4 identified at the B3LYP/6-311++G(2d,2p) level

Quite surprisingly, the binding energies calculated with B3LYP and TPSSH functionals (without empirical dispersion corrections) are higher with the higher-energy isomer than with the low-energy isomer. At the B3LYP/6-311++G(2d,2p) level with MgC₆-12C4 high-energy isomer, Li⁺, Na⁺, and K⁺ binding affinities are 15.83, 10.97, and 8.47 kcal mol⁻¹, respectively, higher than the corresponding MgC₆-12C4 low-energy isomer. On the contrary, in terms of relative stability (after complex formation has occurred), the low-energy isomers of Li⁺, Na⁺, and K⁺ of MgC₆-12C4 are 17.02, 21.87, and 24.36 kcal mol⁻¹, respectively, more stable than their corresponding high-energy counterparts at the B3LYP/6-311++G(2d,2p) level of theory. Likewise, for Be²⁺, Mg²⁺, and Ca²⁺, the binding energies are 55.14, 31.67, and 22.73 kcal mol⁻¹ higher compared to the low-energy host at the same level of theory. It is worth noting here that Be²⁺ ion twists the higher-energy isomer into a tetrahedral form,⁴² which is 22.30 kcal mol⁻¹ lower in energy (see Figure 6) than the non-tetrahedral form. In terms of relative stability, other ions have not shown this reverse trend. The low-energy isomers of Mg²⁺ and Ca²⁺ are 1.16 and 10.10 kcal mol⁻¹, respectively, more stable than their corresponding high-energy isomers. If both the forms of MgC₆-12C4 are kinetically stable, the binding energy values obtained here indicate that the high-energy form (Be²⁺ is an exception here as it reverses the energy trend) can make more stable complexes than

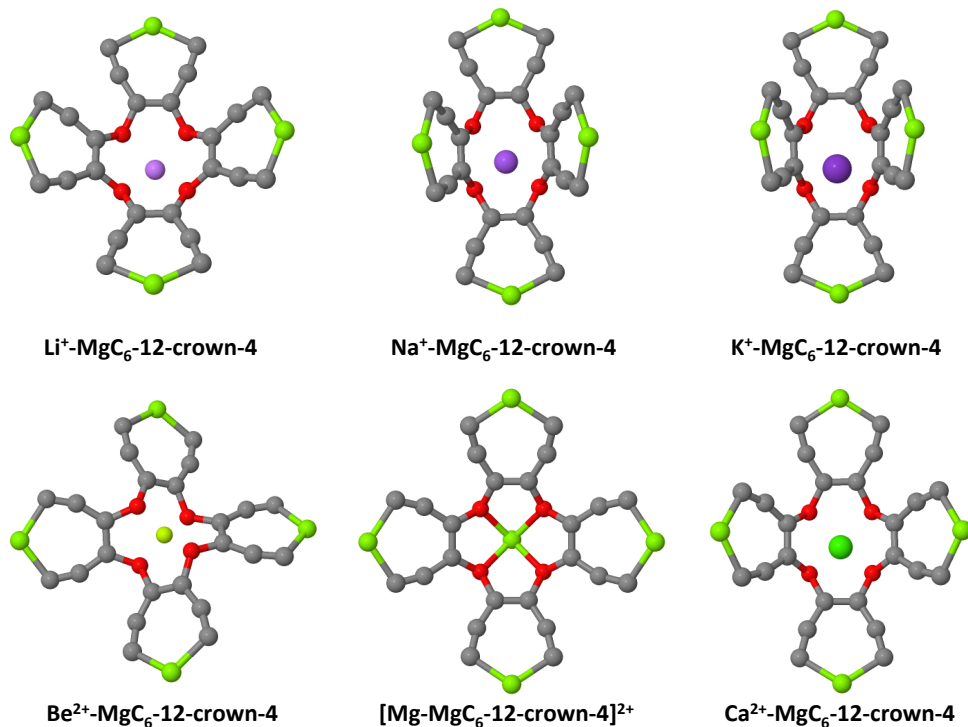


Figure 5: Optimized structures of metal-ion chelated MgC₆-12-crown-4 identified at the B3LYP/6-311++G(2d,2p) level

the low-energy form. As far as Be²⁺ is concerned, encapsulation is highly enhanced when the binding occurs through tetrahedral tetracoordination. With respect to the low-energy isomer, complex formation of Ca²⁺ (Ca²⁺-O bond length is 1.956 Å)⁴³ was also theoretically observed (see Figure 4). However, the binding energies for Ca²⁺ are rather enhanced with the high-energy isomer.

CONCLUSIONS

A brand new series of organomagnesium crown ethers have been theoretically designed using DFT for the first time. Alkali (Li⁺, Na⁺, and K⁺) and alkaline-earth metal-ion (Be²⁺, Mg²⁺, and Ca²⁺) chelated crown ethers have been identified. Binding affinities of these ions with organomagnesium crown ether host molecules have been estimated to gauge their binding strengths. Binding energies are calculated at 0 K whereas the thermally-corrected, ZPVE-inclusive Gibbs free energy values are reported at 298.15 K. These values suggest that Li⁺ ion has the highest binding affinity among the alkali metal ions whereas Be²⁺ ion shows the highest strength among the alkaline-earth metal ions. Compared to normal crown ether molecules in the literature, it is noted here that the binding affinity of Li⁺ ion is low. However, the values are comparable to trioxane derivatives⁴⁰ and dibenzo-14-crown-4 derivatives¹⁸ reported elsewhere. On the other hand, among the alkaline-earth metal ions, the binding strength of Be²⁺ ion is excessively high. Therefore, these host molecules will serve as a better host for alkaline-earth metal ions, in particular Be²⁺, rather than alkali

Table 1: Binding energies (ΔE ; ZPVE inclusive; in kcal mol⁻¹) and Gibbs free energies (ΔG ; in kcal mol⁻¹) of metal-ion chelated organomagnesium crown ethers calculated at different levels^a

host	ion	B3LYP			B3LYP-D3BJ			TPSSh			TPSSh-D3BJ			M06-2X		
		ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	
MgC ₆ ⁻	9C3	Li ⁺	-64.95	-57.40	-68.34	-60.87	-64.21	-66.55	-59.04	-63.42	-55.91					
		Na ⁺	-46.16	-38.49	-50.97	-43.27	-44.85	-48.26	-40.56	-46.32	-38.67					
		K ⁺	-33.54	-26.18	-37.90	-30.53	-32.95	-36.06	-28.75	-35.64	-28.13					
		Be ²⁺	-351.16	-343.26	-355.21	-347.20	-351.88	-344.26	-354.61	-346.91	-337.02	-329.73				
		Mg ²⁺	-207.48	-199.44	-213.16	-204.96	-205.79	-198.10	-209.69	-201.87	-200.18	-192.73				
		Ca ²⁺	-152.19	-144.34	-157.60	-149.74	-153.00	-145.44	-156.66	-149.13	-145.56	-138.12				
12C4 (low)	12C4 (low)	Li ⁺	-62.89	-55.56	-67.97	-60.68	-61.86	-65.49	-58.20	-61.75	-54.71					
		Na ⁺	-44.67	-37.02	-51.18	-43.54	-43.10	-47.83	-40.23	-45.46	-37.84					
		K ⁺	-31.71	-24.33	-37.32	-30.31	-30.87	-35.05	-28.03	-35.20	-27.83					
		Be ²⁺	-345.37	-337.91	-351.49	-344.07	-347.33	-340.19	-351.53	-344.39	-333.35	-326.43				
		Mg ²⁺	-217.71	-209.45	-225.17	-216.93	-216.13	-208.21	-221.34	-213.40	-211.71	-203.97				
		Ca ²⁺	-158.13	-150.04	-165.17	-157.29	-158.48	-150.73	-163.31	-155.70	-153.80	-146.04				
12C4 (high)	12C4 (high)	Li ⁺	-78.72	-71.40	^b	^b	-77.10	^b	^b	^b	^b					
		Na ⁺	-55.64	-47.93	^b	^b	-53.28	^b	^b	^b	^b					
		K ⁺	-40.18	-32.84	^b	^b	-38.71	^b	^b	^b	^b					
		Be ²⁺	-400.51	-392.56	^b	^b	-400.29	^b	^b	^b	^b					
		Mg ²⁺	-249.38	-240.77	^b	^b	-246.26	^b	^b	^b	^b					
		Ca ²⁺	-180.86	-172.80	^b	^b	-180.34	^b	^b	^b	^b					

^a ΔE values are calculated at 0 K. Thermally corrected ΔG values are calculated at 298.15 K. ^b Not calculated at this level of theory. Because, empirical dispersion correction on the host system (i.e., the high-energy isomer) leads to the low-energy isomer upon optimization.

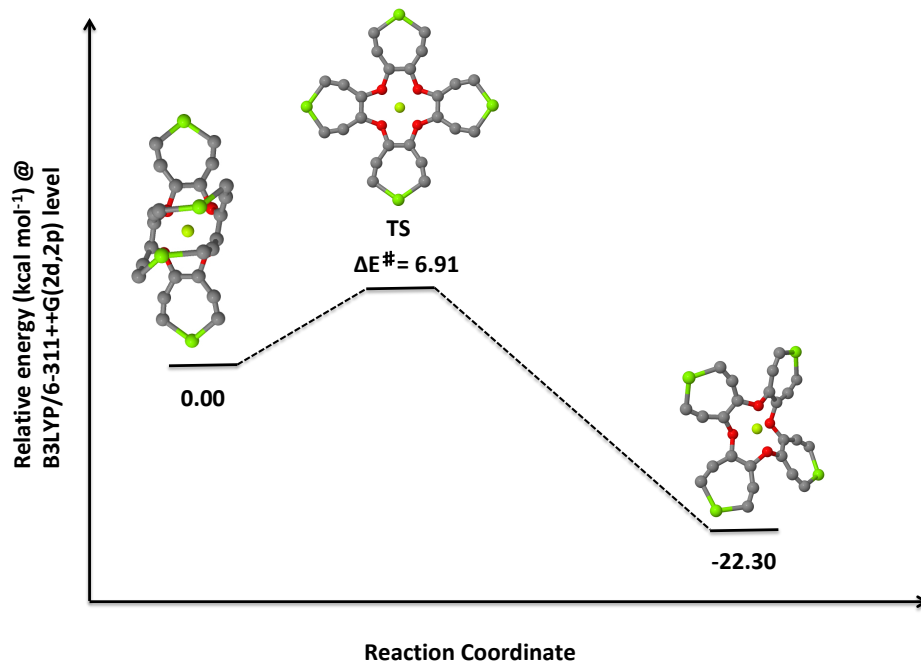


Figure 6: Schematic outline of the energy barrier between the two isomers of $\text{Be}^{2+}\text{-MgC}_6\text{-12C}_4$ at the B3LYP/6-311++G(2d,2p) level

Table 2: Key optimal parameters (in Å and degree) of MgC_6 crown ethers and their complexes calculated at the M06-2X/6-311++G(2d,2p) level

system	C-O	$\text{M}^{+/2+}$ - O	O-O (adjacent)	C=C	$\phi(\text{C-C-O-M}^{+/2+})$
$\text{MgC}_6\text{-9C}_3$	1.376	-	2.716	1.354	-
$\text{Li}^+\text{-MgC}_6\text{-9C}_3$	1.401	1.952	2.647	1.352	-15.46
$\text{Na}^+\text{-MgC}_6\text{-9C}_3$	1.395	2.320	2.682	1.353	-24.30
$\text{K}^+\text{-MgC}_6\text{-9C}_3$	1.391	2.690	2.694	1.354	-30.68
$\text{Be}^{2+}\text{-MgC}_6\text{-9C}_3$	1.453	1.566	2.502	1.356	-3.08
$\text{Mg}^{2+}\text{-MgC}_6\text{-9C}_3$	1.430	1.973	2.651	1.358	-16.48
$\text{Ca}^{2+}\text{-MgC}_6\text{-9C}_3$	1.416	2.281	2.653	1.357	-24.75
$\text{MgC}_6\text{-12C}_4$ (low)	1.362;1.383	-	2.664;2.731	1.356;1.357	-
$\text{Li}^+\text{-MgC}_6\text{-12C}_4$	1.387;1.402	1.938;2.240	2.634;2.608	1.350;1.354	-22.46;31.05
$\text{MgC}_6\text{-12C}_4$ (high)	1.368;1.384	-	2.688;2.739	1.366;1.367	-

metal ions. Further, it is observed that Mg^{2+} ion always makes a chelated complex with various host molecules by directly making a bond with the donor oxygen atoms.

Supporting Information

Cartesian coordinates of the optimized geometries and total electronic energies obtained at different levels are given.

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Conflict of interest

The authors declare that they have no conflict of interest.

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