Flat crown ethers with planar tetracoordinate carbon atoms

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Abstract

Novel flat crown ether molecules have been characterized in silico using DFT hybrid and hybrid-meta functionals. Monomer units of Si_2C_3 with a planar tetracoordinate carbon atom have been used as building blocks. Alkali (Li^+, Na^+, K^+, Rb^+, and Cs^+) and alkaline-earth (Ca^{2+}, Sr^{2+}, and Ba^{2+}) metals, and uranyl (UO_2^{2+}) ion selective complexes have also been theoretically identified. The high symmetry and higher structural rigidity of the host molecules may likely to impart higher selectivity in chelation. Theoretical binding energies have been computed and experimental studies are invited.

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1 Introduction

The concept of molecules with a planar tetracoordinate carbon (ptC)[1,2] atom is an inspiration to all chemists despite it breaks one of the fundamental paradigms of organic chemistry - i.e., tetrahedral tetracoordinate carbon.[3-14] Experimental and theoretical confirmation of pentaatomic ptC species (CAl_4^-, $CAl_3Si^{-/0}$, $CAl_3Ge^{-/0}$, CAl_4^{2-}, etc.,)[15-18] have given some momentum in the search of these molecules in the gas phase. Stabilization of ptC by hydrogenation, in the case of $CAl_4H^{-/0}$, has also been reported recently.[19] The effect of "pt" silicon (ptSi)[20-24] atom in the stability of calix[4]pyrrole hydridosilicate[25] serves as the first experimental proof for ptSi, which motivates the study of these molecules further. Experimentally, it was also demonstrated in the past that molecules with a ptC atom can be enormously stabilized by the cooperative influence of metal pairs (Zr/Al or Zr/Zr$^+$) of atoms.[26] The first crystallographically characterized ptC molecule, a divanadium complex, identified by Cotton and Miller,[27] was recognized later by Keese.[4] It is also noted here that molecules with a planar hypercoordinate carbon (phC)[7,28-38] atom are also actively pursued. Apart from the chemical bonding perspective, interest in molecules with a ptC or phC atom stems from the fact that they could be used as potential new materials.[21,39]

(a) Si$_2$C$_3$-8-crown-2 (D$_{2h}$)   **(b) Si$_2$C$_3$-12-crown-3 (D$_{3h}$)**   **(c) Si$_2$C$_3$-16-crown-4 (D$_{4h}$)**

(d) Si$_2$C$_3$-20-crown-5 (D$_{5h}$)   **(e) Si$_2$C$_3$-24-crown-6 (D$_{6h}$)**
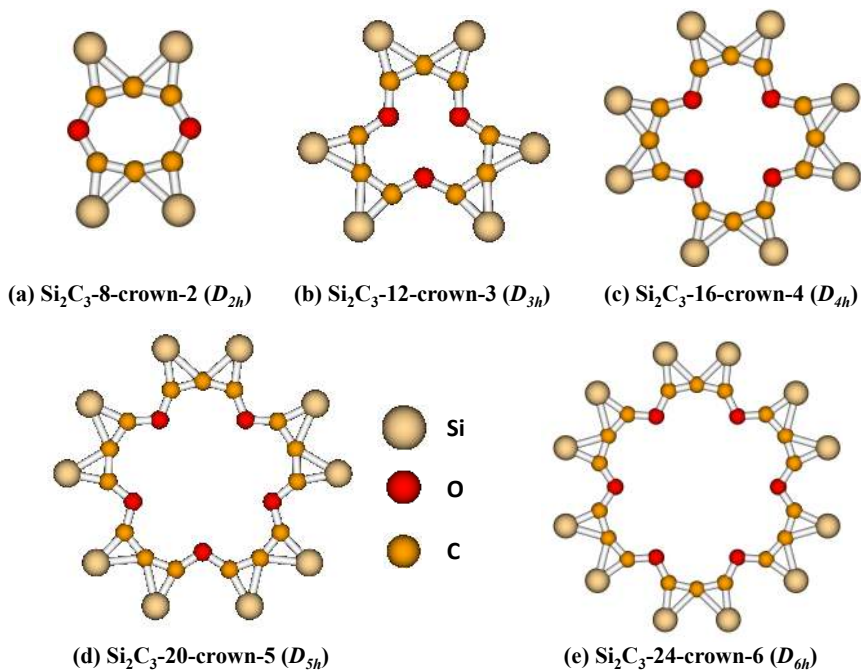
Figure 1: Flat crown ethers of Si_2C_3 with ptC atoms identified at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory.

Pioneering work on crown ethers by Pedersen[40] and Cram,[41] and on cryptands by Lehn[42] marked the birth of a new field called supramolecular chemistry. Whether it is a liquid or gas phase, conventional crown ether molecules characteristically bind different metal cations depending upon the size of the macrocyclic ring, polarity of the medium, and also the type of the donor atom.[43–45] Because of this versatility, more than 10,000 crown ether molecules have been synthetically characterized[46–50] and their potential applications in phase transfer catalysis,[51] chemical separations,[52] analytical methods,[53] and also in nuclear waste management have already been well-documented.[54–56] Motivated by molecules with a ptC atom and also by crown ethers, new "flat crown ether molecules" have been designed here and their chelation behavior have also been explored computationally. Embedding crown ethers in graphene[57] or carbon nanostructures[58] have been emerging to control their low structural rigidity.[59–61] Preorganizing the host molecule to suit the guest is a necessity for its potential applications. Here, instead of using a graphene environment, a novel approach has been followed by taking advantage of the concept of molecules with a ptC atom and consequentially making flat crown ethers to maximize its suitability.

2 Results and Discussion

In this work, utilizing Si_2C_3 with a ptC atom as a base unit, we have computationally identified different flat crown ethers starting from Si_2C_3-8-crown-2 (Si_2C_3-8C2 from here on wards) to Si_2C_3-24-crown-6 (Si_2C_3-24C6), which are depicted in Figure 1. Five different flat metal-chelated complexes identified at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory, Li^+-Si_2C_3-16C4, Na^+-Si_2C_3-16C4, Ca^{2+}-Si_2C_3-16C4, K^+-Si_2C_3-20C5, and Rb^+-Si_2C_3-20C5 are shown in Figures 2 (a), (b), (c), (d), and (e), respectively. Si_2C_3-16C4 also forms a coordinated complex with uranyl ion, UO_2^{2+}-Si_2C_3-16C4, which is shown in Figure 3. For brevity, all optimal geometry parameters collected are shown in the electronic supporting information and the binding energies computed for various metal-chelated Si_2C_3-flat crown ethers including UO_2^{2+} are given in Table 1. In this communication, predominant focus has been paid on Si_2C_3-16C4 and -20C5 and their chelated complexes considering the cavity ring sizes and ionic radii of different metal ions. Metal chelation studies with Si_2C_3-24C6 is currently ongoing and would be the focus of our future work. Starting from Si_2C_3-16C4, as the overall cavity ring size increases (especially diagonal O-O distances), alkali metal ions Li^+ and Na^+, and alkaline-earth metal ion, Ca^{2+}-chelated complexes are possible and they have been identified to be minima using DFT at all levels employed herein. Although K^+ forms a complex with Si_2C_3-16C4, flat structure was found to be a transition state and minimum geometry was found to be in a "quasi plate" shape (see Figure 4). Immediate higher homologue, Si_2C_3-20C5, hosts both K^+ and Rb^+ and retains overall planarity.

From Table 1, the following trend has been observed. As the ionic radii

(a) Li$^+$-Si$_2$C$_3$-16-crown-4   (b) Na$^+$-Si$_2$C$_3$-16-crown-4   (c) Ca^{2+}-Si$_2$C$_3$-16-crown-4

M$^+$--O distance (Å)
(a) Li$^+$ --O = 2.203
(b) Na$^+$ --O = 2.299
(c) Ca^{2+} --O = 2.324
(d) K$^+$--O = 3.044
(e) Rb$^+$--O = 3.076

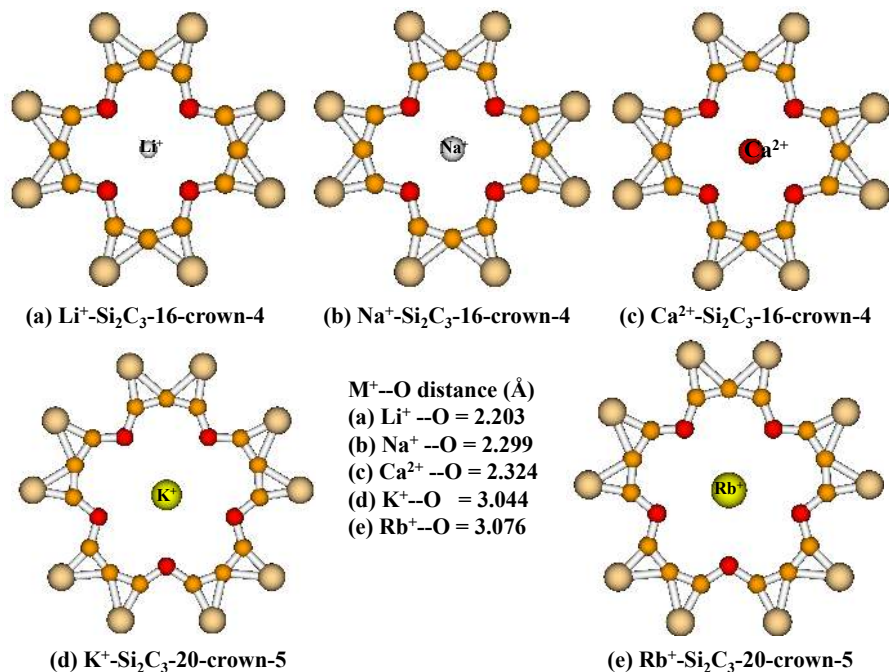(d) K$^+$-Si$_2$C$_3$-20-crown-5   (e) Rb$^+$-Si$_2$C$_3$-20-crown-5

Figure 2: Five different M$^+$-chelated Si$_2$C$_3$ crown ethers identified at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory.

Table 1: Binding energies (in eV) of flat Si$_2$C$_3$ metal-chelated crown ethers calculated at different levels.

Species	Symmetry; State	PBE0	B3LYP	B3LYP-D3BJ	TPSSh	TPSSh-D3BJ
				6-311++G(2d,2p)		
Li$^+$-Si$_2$C$_3$-16C4	$^1A_{1g}$; D_{4h}	-3.22	-3.44	-3.80	-3.16	-3.43
Na$^+$-Si$_2$C$_3$-16C4	$^1A_{1g}$; D_{4h}	-2.51	-2.75	-3.16	-2.46	-2.74
K$^+$-Si$_2$C$_3$-16C4[a]	$^1A_1$; C_{4v}	-1.59	-1.81	-2.22	-1.61	-1.91
Rb$^+$-Si$_2$C$_3$-16C4[a]	$^1A_1$; C_{4v}	-1.19	-1.37	-1.78	-1.20	-1.51
Cs$^+$-Si$_2$C$_3$-16C4[a]	$^1A_1$; C_{4v}	-0.96	-1.12	-1.52	-0.99	-1.28
Ca^{2+}-Si$_2$C$_3$-16C4	$^1A_{1g}$; D_{4h}	-7.88	-8.23	-8.76	-7.82	-8.19
Sr^{2+}-Si$_2$C$_3$-16C4[a]	$^1A_1$; C_{4v}	-5.77	-6.17	-6.70	-5.79	-6.15
Ba^{2+}-Si$_2$C$_3$-16C4[a]	$^1A_1$; C_{4v}	-4.70	-5.11	-5.68	-4.79	-5.19
K$^+$-Si$_2$C$_3$-20C5	$^1A_1'$; D_{5h}	-1.92	-2.08	-2.54	-1.86	-2.21
Rb$^+$-Si$_2$C$_3$-20C5	$^1A_1'$; D_{5h}	-1.62	-1.82	-2.31	-1.61	-1.97
Cs$^+$-Si$_2$C$_3$-20C5[a]	$^1A_1$; C_{5v}	-1.32	-1.51	-1.99	-1.33	-1.68
[UO$_2$-Si$_2$C$_3$-16C4]$^{2+}$	$^1A_{1g}$; D_{4h}	-9.02	-9.39	-10.33	-9.28	-9.95

[a] This M$^+$-chelated structure is not completely flat.

increases down the group, binding energy decreases. While Li$^+$ and Na$^+$ make a chelated complex with Si$_2$C$_3$-16C4 and retains planarity, K$^+$, Rb$^+$, and Cs$^+$ do not maintain planarity in minimum energy geometries though binding occurs. This is not surprising due to the fact that ionic radii increases further

from Na^+ to K^+. However, due to higher structural rigidity, the host molecule is unable to accommodate K^+ ion inside the cage (see Figure 4). Consequently, the electrostatic interactions between K^+ and four oxygen atoms push the entire molecule like a "quasi plate". Similar structures have been obtained for Rb^+ and Cs^+ in chelation with Si_2C_3-16C4 (not shown here for brevity). Moving to higher homologue, Si_2C_3-20C5, when Li^+ and Na^+ ions remain at the center, they become higher-order saddle points (see supporting information for details). However, K^+ binds with this host molecule (see Figure 2) due to slightly increased ring size now and the binding energies are in the range of -1.86 to -2.54 eV. Perhaps, though there are five oxygen donor atoms now, the binding energy is still slightly larger (-2.54 eV) compared to the lower homologue (-2.22 eV) at the same level of theory (B3LYP-D3BJ/6-311++G(2d,2p); see Table 1). Indirectly, this feature imposes higher selectivity. Also, this indicates that the electrostatic interactions are stronger when planarity is maintained. Rb^+ also binds with Si_2C_3-20C5. Here, it maintains planarity unlike Rb^+-Si_2C_3-16C4. The binding energies are in the range of -1.61 to -2.31 eV for Rb^+-Si_2C_3-20C5. Just like K^+ ion, binding energies are slightly larger for Rb^+ (despite 5 donor atoms now instead of 4) when the entire molecule is in one plane. With Cs^+, binding occurs with Si_2C_3-20C5 but planarity is no longer maintained.

As far as alkali-earth metals are concerned, when Be^{2+} remains at the center in Si_2C_3-16C4, all the calculations at different levels lead to multiple number of imaginary frequencies. On the contrary, Mg^{2+} with Si_2C_3-16C4 makes covalent bonds with oxygen atoms but that geometry eventually turned out to be a second-order saddle point at all levels (see supporting information). However, the next ion Ca^{2+}, whose ionic radii (114 pm) is comparable to Na^+ (116 pm), binds with Si_2C_3-16C4. Due to higher charge and also being in planar configuration, the binding energies are sufficiently high (-7.82 to -8.76 eV; see Table 1) for Ca^{2+}-Si_2C_3-16C4. Sr^{2+} and Ba^{2+} also bind with the latter, however, planarity is lost yet again due to increased ionic radii. Also, their binding energies are comparably less compared to Ca^{2+}. Our investigation is currently ongoing with respect to binding tendencies of alkali-earth metal ions in Si_2C_3-20C5. It is noted here that Si_2C_3-16C4 also forms a complex with uranyl ion, $[UO_2$-Si_2C_3-$16C4]^{2+}$ (see Figure 3). The reason we had tried this particular ion is largely due to the fact that enormous amount of effort had already been devoted in making new chelating agents for UO_2^{2+}[62,63]. into uranyl oxides. Here, we are proposing a new chelating agent for UO_2^{2+} whose binding energies are in the range of -9.02 to -10.33 eV.

The optimal geometry parameters of various flat crown ethers are collected in the ESI†. The ptC-C and ptC-Si bond lengths show single bond characteristics. Also, quite consistently, the Si-C bond length exhibits double bond characteristics (~ 1.75 Å) in all cases. The optimized geometries of neutral flat crown ethers and their chelated complexes identified here are of same symmetry when planarity is maintained. In all cases, the ground electronic states are singlets and they are non-degenerate. Thus, they are not Jahn-Teller distorted[64] within their ground electronic states.
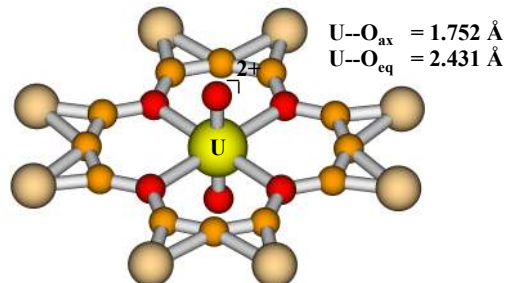
U--O_{ax} = 1.752 Å
U--O_{eq} = 2.431 Å

Figure 3: [UO$_2$-Si$_2$C$_3$-16-crown-4]$^{2+}$ identified at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory.

(a) top-view   **K$^+$--O = 2.708 Å**   **(b) bottom-view**
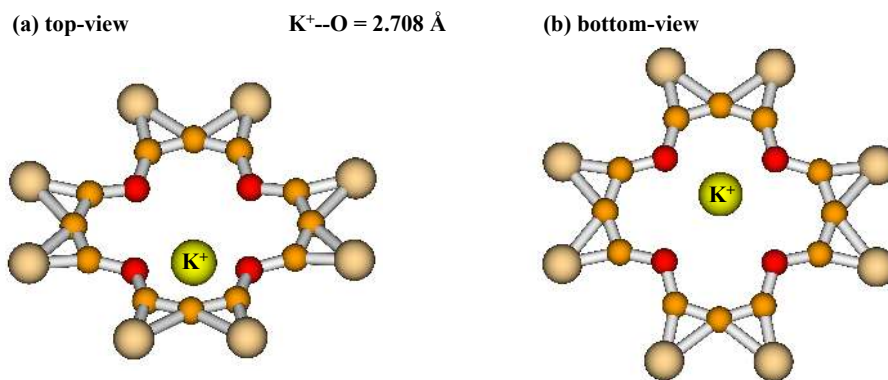

Figure 4: Two different views of K$^+$-Si$_2$C$_3$-16-crown-4 identified at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory are shown.

3   Conclusions

In conclusion, a new series of crown ether molecules called "flat crown ethers" have been computationally characterized using the advent of molecules with a ptC atom. This novel approach opens up a new direction in the area of already popular "supramolecular chemistry". The synthetic possibilities of these molecules are invited and there are ample amount of reasons why one should study these molecules considering their higher degree of selectivity in metal chelation and also symmetry. Chelation with UO_2^{2+} is certainly encouraging to study these molecules further. Perhaps, only time shall tell what kind of potential applications or further new avenues are possible with these peculiar molecules.

4   Computational Details

Initially geometry optimization and frequency calculations have been done using density functional theory (DFT) with two different hybrid-functionals, PBE0[65] and B3LYP[66–68] with the 6-311++G(2d,2p) basis set.[69,70] All minima obtained at these latter levels have been reoptimized including Grimme's empirical dispersion corrections (D3)[71] with Becke-Johnson damping (D3BJ),[72,73] to make sure whether the wavefunction is stable or not. Further, all geometries have also been optimized with the TPSSh[74] hybrid-meta functional including D3BJ corrections. All the flat crown ethers studied here are found to be stable at these five different levels of theory. For Rb^+-, Cs^+-, Sr^{2+}-, and Ba^{2+}-chelated crown ethers, calculations have been done with the LANL2DZ ECP (for metal ion alone).[75] For uranium, Stuttgart/Dresden ECP of MWB60[76] and the corresponding atomic natural orbital basis set[77] have been used in all calculations. All electronic structure calculations have been done with the Gaussian program package[78].

5   Supporting Information

Cartesian coordinates of the optimized geometries, total electronic energies, zero-point vibrational energies (ZPVEs), ZPVE-corrected total energies, number of imaginary frequency values, and optimal geometry parameters obtained at different levels are given.
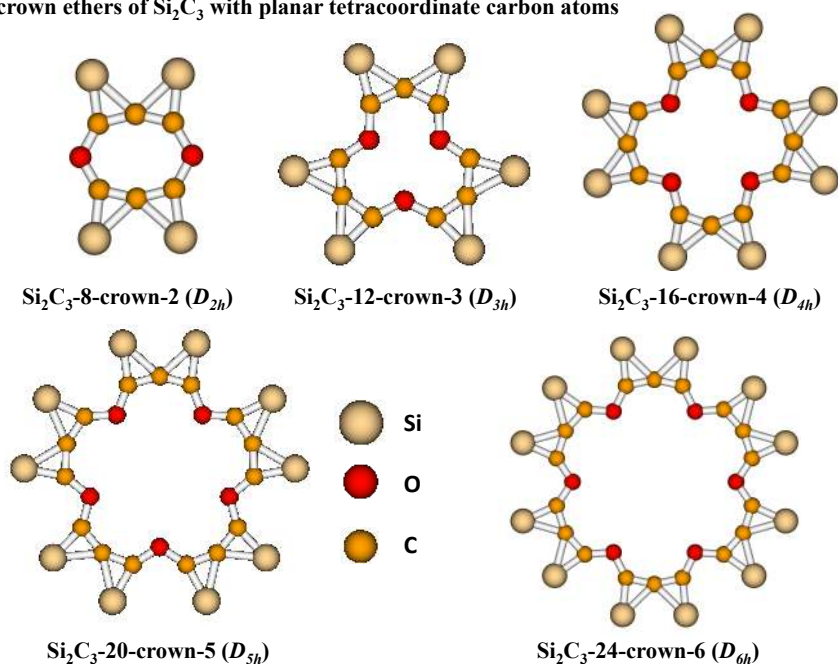
6   Acknowledgment

7   Keywords

alkali metals, alkaline-earth metals, crown compounds, chelates, host-guest molecules, planar tetracoordinate carbon, uranyl (UO_2^{2+}) ion.

8   TOC

Novel flat crown ether molecules containing planar tetracoordinate carbon atoms (see picture 8) have been theoretically characterized using Si_2C_3 units as building blocks.

Flat crown ethers of Si_2C_3 with planar tetracoordinate carbon atoms

Si₂C₃-8-crown-2 (D_{2h})   Si₂C₃-12-crown-3 (D_{3h})   Si₂C₃-16-crown-4 (D_{4h})

Si₂C₃-20-crown-5 (D_{5h})   Si₂C₃-24-crown-6 (D_{6h})

Si
O
C

9 Conflict of Interest

The authors declare no conflict of interest.

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