



D_{3h} $X_3Li_3^+$ (X = C, Si and Ge): Superalkali cations containing three planar tetracoordinate X atoms



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ABSTRACT

A new class of superalkali cations $X_3Li_3^+$ (X = C, Si and Ge) containing three planar tetracoordinate X atom have been characterized using ab initio methods. These perfect planar high-symmetric (D_{3h}) species are the global minimum of the systems based on extensive stochastic structural searches, followed by high level quantum chemistry calculations. The vertical electron affinities (VEAs) of the $X_3Li_3^+$ cations range from 2.88 to 3.02 eV at OVGF//MP2/6-311+G(3df) level, which are lower than 3.89 eV of Cs atom. Thus, they represent the first series of superalkali cations with three ptX (X = C, Si and Ge) atoms. Bonding analyses reveal that there are mainly ionic bonds between X and Li atoms, while there are covalent bonds between X atoms. AdNDP, NICS analyses indicate that $X_3Li_3^+$ (X = C, Si and Ge) cations are π aromatic with two delocalized π electrons. Large HOMO–LUMO energy gaps 7.62–10.41 eV further support their thermodynamic stability. Born–Oppenheimer molecular dynamics (BOMD) investigations indicate that the structures of these ptX species are well maintained during 20 ps simulations. The current results may motivate theoretical and experimental studies on novel ptX (X = C, Si and Ge) complexes as well as superalkali species.

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1. Introduction

Planar tetracoordinate carbon (ptC), that is, the carbon atom coordinated by four ligands in a planar arrangement, was first introduced by Monkhorst [1]. In 1970, Hoffmann et al. suggested the “electronic” and “mechanical” strategies to stabilize the ptC center [2]. The first stable ptC molecule, 1,1-dilithiocyclopropane was theoretically predicted by Schleyer and Popleld [3]. Since then, considerable and continuous efforts had been devoted to the design, prediction, and production of planar tetracoordinate carbon (ptC) complexes in the past four decades. It should be noted that some stable anti-vant Hoff/LeBel compounds including $V_2(2,6\text{-dimethoxyphenyl})_4$, $Ca_4Ni_3C_5$, and $CP_2Zr(\mu\text{-}\eta^1, \eta^2\text{-Me}_3SiCCPh)(\mu\text{-Cl})AlMe_2$ with the ptC centers were observed by X-ray crystallography [4–7]. In particular, several pentaatomic ptC species including Al_4C^- , $CaAl_3Si^-$, and $CaAl_3Ge^-$ with 17 and 18 valence electrons, were experimentally detected in the gas phase via photoelectron spectroscopy (PES) in 1998–2000 [8–10]. Planar tetracoordinate silicon (ptSi) and germanium (ptGe) were also experimentally observed in C_{2v} MAl_4 and MAl_4^- (M = Si, Ge) with 16 and 17 valence electrons by Wang's group [11]. Very recently,

the pentaatomic ptSi species with 14 valence electrons were systematically investigated by Xu and Ding [12]. Most of other theoretical and experimental works on ptC species and their analogues had been summarized in several exhaustive and comprehensive reviews [13–17].

As the extension, the species containing multiple ptXs (X = C, Si and Ge) had also been designed and investigated with theoretical methods. In 2004, D_{3h} $C_6H_6^{2+}$ containing three ptC atoms was predicted by Priyakumar and Sastry [18]; in 2005, a series of planar aromatic clusters (including C_2B_8 , $C_3B_9^{3+}$, and $C_5B_{11}^+$) with multiple ptCs were designed by Schleyer and coworkers [19]; in 2007, using the Ni_4H_4C [20] as the building block, the one-, two- or three-dimensional crystals with multiple ptCs were predicted by Wu et al. [21]. In addition, the planar or quasi-planar B_2C , C_2Si , Ni_2C two dimensional crystals containing multiple ptX (X = C, Si and Ge) atoms had been theoretically investigated [22–24].

However, the majority of the previous studies on ptX (X = C, Si and Ge) molecules focus on their structures and bonding characters. In this work, we shall introduce a new dimension of novelty to the ptX (X = C, Si and Ge): ptX complexes that behave as superalkali cations. Superalkalies with an ionization potential (IP) lower than the cesium atom (3.89 eV), [25] were first proposed by Gutsev and Boldyrev [26]. Superalkalies can be designed using the alkalization and halogenation strategies [27]. Using the two strate-

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gies, a number of mononuclear, binuclear, and polynuclear superalkalies with considerably low vertical detachment energies (VDEs), or their cations with low vertical electron affinities (VEAs), were theoretically designed or experimentally characterized in the past 30 years. Such as OLi_3 , $\text{M}_2\text{Li}_{2k+1}^+$ ($\text{M} = \text{F}, \text{O}, \text{N}, \text{C}, \text{B}$ for $k = 1, 2, 3, 4, 5$, respectively), and YLi_4^+ ($\text{Y} = \text{PO}_4, \text{AsO}_4, \text{VO}_4$) [28–30]. However, the central nonmetal atoms in these superalkalies were almost coordinated by ligands in a non-planar fashion. Recently, we found that the global minimum of CBe_5H_5^+ contained the quasi-planar pentacoordinate carbon and had the low VEA value (4.1 eV), which could be considered as the ppC pseudo-alkali metal cation [31]. Can superalkalies contain the planar tetracoordinate carbon, silicon and germanium atoms? The answer appears to be “yes”.

In this work, we report on a new series of superalkali cations X_3Li_3^+ ($\text{X} = \text{C}, \text{Si}$ and Ge) with three ptX atoms. These novel species with 14 valence electrons turned out to be the global minima of the systems via the extensive structural searches. Chemical bonding in the series features π aromaticity with 2π electrons, conforming to the $(4n + 2)$ Hückel rule. It is most important for X_3Li_3^+ ($\text{X} = \text{C}, \text{Si}$ and Ge) that they have low VEAs (2.88–3.02 eV). It should be noted that the most stable form of C_3Li_3^+ was reported by Jemmis et al. [32]. However, its superalkali character was not studied or recognized. To the best of our knowledge, there have been no studies to date on ptX ($\text{X} = \text{C}, \text{Si}$ and Ge) species with superalkali properties. The present computational studies provide a critical extension to the fields of the planar tetracoordinate nonmetal atoms and the superalkali chemistry.

2. Computational methods

The potential energy surfaces of X_3Li_3^+ ($\text{X} = \text{C}, \text{Si}$ and Ge) were explored using the gradient embedded genetic algorithm (GEGA) procedure [33] at the B3LYP/3-21G level [34,35]. After the initial search, the candidate low-lying structures were re-optimized at the MP2/6-311+G(3df) level [36]. Vibrational frequencies were carried out to check whether the optimized structures are true minima or saddle points. To obtain more accurate relative energies, high level single-point calculations for the four lowest-isomers (at MP2 level) were further carried out at the CCSD(T)/6-311+G(3df) level [37,38]. The relative energies of isomers were determined by the CCSD(T)/6-311 + G(3df) energy including the MP2/6-311 + G(3df) zero-point energy corrections. To gain insight into the bonding characters of these planar species, natural bond orbital (NBO), molecular orbitals (MOs) and adaptive nature density partitioning (AdNDP) analyses [39,40] were performed at MP2/6-311+G(3df) and MP2/6-31G levels, respectively. To assess the aromatic nature of these ptX species, the nucleus independent chemical shifts (NICS) [41–43] were calculated above 1 Å of the centers three-membered rings. The vertical electron affinities (VEA) and vertical detachment energies (VDEs) for X_3Li_3^+ ($\text{X} = \text{C}, \text{Si}$ and Ge) were calculated with the outer valence Green's function (OVGF) [44]. All calculations in this work were performed using the Gaussian 09 package [45], except for AdNDP analyses. Molecular structures and molecular orbitals were visualized using the CYLview [46] and Molekel 5.4 [47] program, respectively.

3. Results and discussion

3.1. Geometrical structures

It should be noted that the X_3 three-membered rings are well maintained in these low-lying isomers (**1A–3D**, except for **1C**). Generally, there are three ways for Li atoms to bond with C, Si, Ge: terminal μ^1 -Li, bridging μ^2 -Li and face-capping μ^3 -Li. Our

calculations at MP2/6-311+G(3df) level revealed high preference of the bridging μ^2 -Li. As shown in Fig. 1, the perfect planar D_{3h} C_3Li_3^+ (**1A**), Si_3Li_3^+ (**2A**), and Ge_3Li_3^+ (**3A**) with the bridging μ^2 -Li atoms are all the global minima on their potential energy surfaces at CCSD(T)//MP2/6-311+G(3df) level, which are 9.98, 14.90, and 13.57 kcal/mol lower than corresponding second lowest isomers **1B**, **2B**, and **3B**, respectively. There are two important factors for the stability of X_3Li_3^+ ($\text{X} = \text{C}, \text{Si}$ and Ge): one is the numbers of the bridging μ^2 -Li atoms; the other is the co-planarity of whole structure. There are some differences between C_3Li_3^+ and Si_3Li_3^+ , Ge_3Li_3^+ for the bigger electro-negativity of C than that of Si and Ge. The co-planarity of whole structure is one important factor for the stability of the isomers of C_3Li_3^+ . The non-planar isomer **1D** is far less stable than planar **1A**, **1B** and **1C**. Obviously, the numbers of the bridging-Li atoms for Si_3Li_3^+ and Ge_3Li_3^+ are more important for their stability than C_3Li_3^+ . As shown in Fig. 1, for Si_3Li_3^+ and Ge_3Li_3^+ , the second lowest isomers for **2B** and **3B** contain three bridging μ^2 -Li atoms, while isomer **2C** and **3C** contain two bridging μ^2 -Li atoms and one terminal μ^1 -Li atoms. **2A** and **3A** are more stable than **2B** and **3B** mainly due to their perfect planarity. According to the literatures, the most stable structures for both Si_3H_3^+ and Si_3Au_3^+ possess perfect planar triangle with three terminal H and Au, respectively [48,49]. Given the C/Si/Ge and H/Au/Li analogy, it is easy to design the D_{3h} X_3Li_3^+ with three terminals μ^1 -Li atoms. However, as shown in Fig. 1, **1B** and **2D** turn out to be only the local minima lying 9.98 and 19.97 kcal/mol higher in energy than the **1A** and **2A** at CCSD(T)//MP2/6-311+G(3df) level. It should be noticed that D_{3h} Ge_3Li_3^+ with three terminal μ^1 -Li atoms turns out to be the transitional state with one imaginary frequency ($42i \text{ cm}^{-1}$). Relaxation of it along the imaginary a_2' mode leads to the stable **3A**. Thus, **1A**, **2A** and **3A** are all most stable in thermodynamics.

In terms of bond distances, the C–C, Si–Si and Ge–Ge bond length of C_3Li_3^+ (**1A**) 1.428 Å, Si_3Li_3^+ (**2A**) 2.321 Å and Ge_3Li_3^+ (**3A**) 2.486 Å at MP2/6-311+G(3df) level, are some shorter than typical C–C, Si–Si and Ge–Ge covalent single bonds, respectively, suggesting that there are partial double bonds characters between them. The C–Li, Si–Li and Ge–Li bond length of C_3Li_3^+ 2.033 Å, Si_3Li_3^+ 2.611 Å and Ge_3Li_3^+ 2.668 Å are normal X–Li ($\text{X} = \text{C}, \text{Si}$ and Ge) bonds, respectively.

3.2. Bonding characteristics

The stabilities of these ptC species X_3Li_3^+ ($\text{X} = \text{C}, \text{Si}$ and Ge) are mainly determined by two kinds of force: one is the covalent interactions between the X atom and its neighbors; the other is the ionic bonding between X and Li atoms. Nature bond orbital (NBO) analyses help us to understand the bonding nature of these novel species. All X atoms carry negative charges in X_3Li_3^+ ($\text{X} = \text{C}, \text{Si}$ and Ge) and the Li atoms carry positive charges, respectively. It should be noted that there are considerable charges transfer from the peripheral Li atoms to the central electronegative X atom in these ptC species **1A–3A**. Each X atom carries the negative charges -0.49 to $-0.57 |e|$ and each Li carries the positive charges $+0.82$ to $+0.90 |e|$ in **1A–3A**. The covalent bonding in **1A–3A** is dominated by X–X, with wiberg bond orders of 1.18–1.43. The $\text{WBI}_{\text{X-Li}}$ values 0.09–0.12 indicate that there are mainly ionic bonding between X and Li atoms. In addition, the total WBIs of C, Si, Ge and Li atoms are also in agreement with the above analysis.

In order to further understand the electronic structures of these interesting planar species, molecular orbital analyses were performed. The LUMO and the valence molecular orbitals of X_3Li_3^+ ($\text{X} = \text{C}, \text{Si}$ and Ge) (**1A–3A**) are plotted in Fig. 2. As shown in

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