

In silico search for planar hexacoordinate Silicon atom: A kinetically viable species

Amlan J. Kalita, Shahnaz S. Rohman, Chayanika Kashyap, Sabnam S. Ullah, Indrani Baruah,
Lakhya J. Mazumder and Ankur K. Guha*

*Advanced Computational Chemistry Centre, Department of Chemistry, Cotton University,
Panbazar, Guwahati, Assam, INDIA-781001.*

*E-mail: ankurkantiguha@gmail.com

Abstract

In silico search for planar hexacoordinate silicon center has been initiated by global minimum screening with density functional theory and energy refinement using coupled cluster theory. The search resulted in a local minimum of $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$ structure which contains a planar hexacoordinate silicon center (phSi). The phSi structure is 5.8 kcal/mol higher in energy than the global minimum. However, kinetic studies reveal that the local minimum structure has enough stability to be detected experimentally. Born-Oppenheimer molecular dynamics (BOMD) simulations reveal that the phSi structure can be maintained up to 400 K. The formation of multiple bonds between the central silicon atom and framework aluminium atom is the key stabilizing factor for the planar structure.

Keywords: Hexacoordinate Silicon; kinetically stable; theoretical

Introduction

Soon after the exploration of the strategies to stabilize planar tetracoordinated carbon (ptC),¹ a plethora of studies have been reported which includes planar hypercoordinate first row main group elements such as boron and carbon.²⁻²² For example, the Schleyer and coworkers computationally reported the extended coordination of carbon such as planar penta (ppC) in hyparenes²³ and planar hexa (phC) carbon in CB_6^{2-} .¹⁰ This attracted attention of different groups to design ppCs, however, most of them are experimentally unlikely owing to their local minimum nature of the stationary point on the potential energy surface (PES). The first true global minimum containing a ppC was reported in CAI_5^+ .²⁴ Subsequently, it was shown that replacement of Al atoms in CAI_5^+ by other electropositive elements lead to a

range of ppCs and quasi-ppCs.²⁵ Thus, it seems that electronic balance of the ligand framework is an effective way to stabilize planar hypercoordinate species more than the 18-electron rule.²⁶⁻²⁸ For example, very recently, a ppC with 17-electron, CBe_5H_4^+ , was reported to be global minimum.¹¹ The strategy of ligand electronic balance has also been shown to stabilize planar hexacoordinate boron (phB) by us and others.²²

Although the non-classical structural pattern for carbon has been explored in large number, heavier silicon atom received much less attention. Due to the advantage of silicon over carbon in synthesizing 2D materials,²⁹ exploration of planar hypercoordinate silicon species is worthy. After the first identification of the existence of planar tetracoordinate silicon (ptSi) centre in orthosilicic acid ester in 1979,³⁰ it then served as the building block of conjugated system. Subsequently, a ptSi system, $\text{SiAl}_4^{0/-}$ was reported experimentally and computationally.³¹ Some global minima in ptSi and ptGe systems were reported.³² In 2014, a monolayer containing planar hexacoordinate silicon (phSi) was predicted by Yang and coworkers³³ and later synthesized by Feng and coworkers.³⁴ Some theoretical studies suggested planar pentacoordinate silicon (ppSi) in two dimensional networks.³⁵ Recently, ppSi global minimum is reported in XMg_4Y^- ($\text{X} = \text{Si}, \text{Ge}$; $\text{Y} = \text{In}, \text{Tl}$) and SiMg_3In_2 systems.³⁶ Although some evidence of phSi system are reported in embedded system, but at the molecular regime, there is no evidence of a cluster containing phSi as the most favourable energy structure. Herein, we report an in silico search for a planar hexacoordinate silicon (phSi) system, $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$. The reported cluster is thermodynamically and dynamically very stable and hence, an experimentally viable species.

Various studies have shown that group 13 elements such as B and Al are suitable for stabilizing planar hypercoordinate species.^{24,25} Similar promises has also been shown by alkaline earth metals.²² Thus, we explored the combination of group 13 element with alkaline earth metals to obtain phSi and phGe centres. We started our search with some mixed clusters, $\text{SiB}_3\text{Be}_3^+$ and $\text{SiAl}_3\text{Be}_3^+$ (Figure 1). The planar form of these structures was found to be saddle point on the PES. The smaller size of Be may not be an appropriate choice to circumscribe the silicon and germanium atoms in the same plane. We, therefore, tried with $\text{SiAl}_3\text{Mg}_3^+$ clusters. Interestingly, the planar form of $\text{SiAl}_3\text{Mg}_3^+$ clusters is also a saddle point on PES. Normal mode analysis reveals that one of the Mg atom tries to go away from the molecular plane. We, therefore, envisioned that movement of the Mg atom from the molecular plane can be circumvented by making H-bridges. It is to be noted that H-bridged Be clusters have found promising utility in stabilizing planar hypercoordinate species.^{11,22}

Indeed, the planar $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$ cluster is a local minimum which may be a promising candidate for a global minimum. However, the planar $\text{GeAl}_3\text{Mg}_3\text{H}_2^+$ is a first order saddle point which might be due to larger size of germanium atom. We therefore, carried out extensive searches on the PES for $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$ cluster. To do that, we used ABCluster code^{37,38} to generate possible isomers using M06-2X/TZVP level of theory.³⁹ Low lying isomers were then fully optimized using M06-2X/Def2-TZVP level of theory and the energy refinement were done by running single point calculations at CCSD(T)/Def2-TZVP⁴⁰ over the M06-2X optimized geometries. The PES is scanned for both singlet and triplet states. All energies, hereafter, are reported at CCSD(T)/Def2-TZVP//M06-2X/Def2-TZVP level, unless otherwise noted. All these calculations were performed using Gaussian16 suite of program.⁴¹

Figure 2 shows the minimum energy structures of $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$ cluster. The phSi structure adopts C_{2v} symmetry with singlet electronic ground state (the triplet state is 15.4 kcal/mol higher in energy). It is to be noted that the PhSi structure is not the global minimum. It lies only 5.8 kcal/mol higher in energy than the global minimum. Substitution of H atoms in $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$ by Li, Cu, Ag, Au led to local minimum phSi structures (Figure S1).

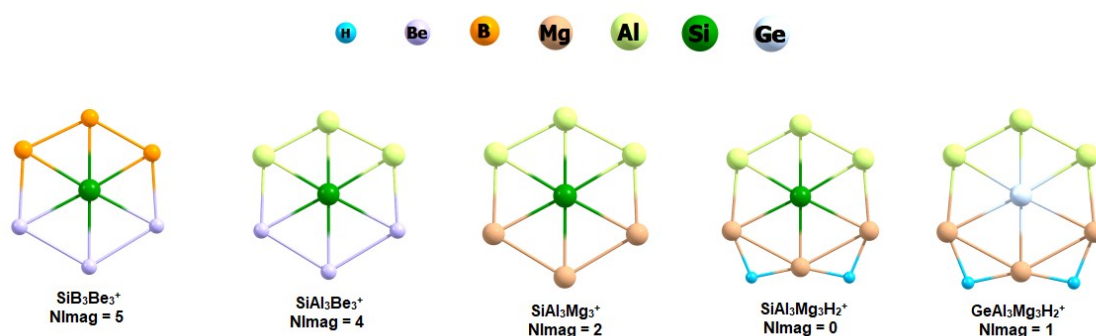


Figure 1. Structures of the mixed clusters. NImag refers to number of imaginary frequencies.

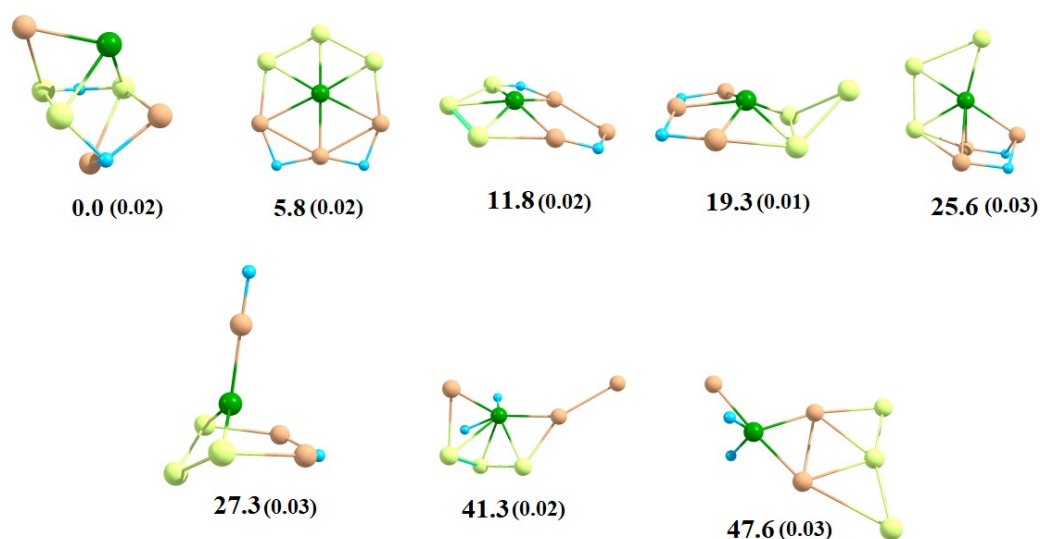
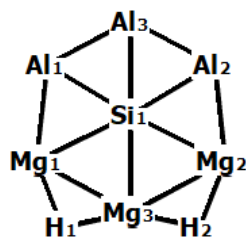


Figure 2. Relative energies (kcal/mol) of the low lying isomers calculated at CCSD(T)/Def2-TZVP//M06-2X/Def2-TZVP level of theory. T_1 diagnostic values are given in parenthesis.

The phSi structure has two equal Si-Al bond lengths (2.57 Å) and one shorter Si-Al bond lengths of 2.46 Å (Table 1). There are two equal Si-Mg bond lengths of 2.77 Å and one shorter Si-Mg bond length of 2.58 Å. The nature of the bonding in phSi structure of $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$ cluster was analyzed using natural bond orbital (NBO)⁴² analysis, quantum theory of atoms in molecules (QTAIM)⁴³ and electron localization function (ELF).⁴⁴ QTAIM and ELF analyses were carried out using Multiwfn program code.⁴⁵ Figure 3 shows the frontier Kohn-Sham orbitals, 2D plot of the laplacian of electron density and electron localization function. HOMO and HOMO-1 represent the Si-Al and Si-Mg σ bonding molecular orbitals (MOs) while HOMO-2 represents the delocalized π MO over the six membered ring. Si-Al bonds have partial double bond character as evidenced by the Wiberg bond index (WBI) values (0.77-0.85) while the Si-Mg bonds are single and weak (Table 1). The Si-Al and Si-Mg bonds should be characterized as polar covalent as revealed by the positive value of the laplacian and negative value of the total electronic energy density.⁴⁶ Interestingly, Si-Al bonds have ellipticity greater than zero signifying partial double bond character.⁴³ The laplacian plot as well as the ELF plot reveal electron delocalization throughout the six membered ring. We, therefore, envisioned that the cluster may show some degree of aromaticity. Nucleus independent chemical shift (NICS)⁴⁷ calculations were then performed. Figure 4 shows the NICS results. Surprisingly, NICS results show marked difference than bonding analyses. NICS results indicate diminished cyclic delocalization as

opposed to bonding analyses. Similar situation is also observed in a recent study on ppSi molecules, SiMg₄In⁻ and SiMg₃In₂.³⁶

Table 1. Bond lengths r (Å), Wiberg bond index (WIB, in parenthesis), electron density (ρ) at the bond critical points, Laplacian of electron density ($\nabla^2\rho$), total electronic energy density ($H(r)$), ellipticity (ε) and natural charges (q) in |e|. All other values are in a.u.



Bonds	r	ρ	$\nabla^2\rho$	$H(r)$	ε	q
Si1-Al1	2.57 (0.77)	0.04	0.06	-0.01	0.32	0.01
Si1-Al2	2.46 (0.85)	0.06	0.08	-0.03	0.21	0.32
Si1-Al3	2.57 (0.77)	0.04	0.06	-0.01	0.32	0.01
Si1-Mg1	2.77 (0.07)	0.03	0.08	-0.01	0.21	1.35
Si1-Mg2	2.58 (0.20)	0.05	0.09	-0.01	0.23	1.56
Si1-Mg3	2.77 (0.07)	0.05	0.08	-0.01	0.21	1.35

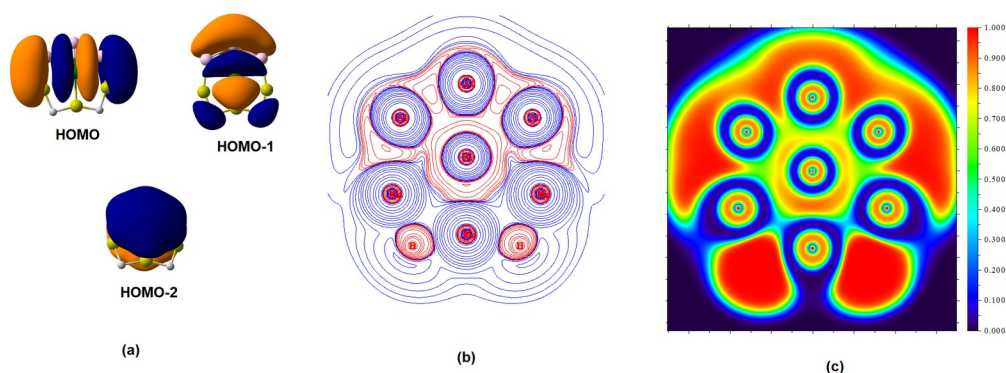


Figure 3. (a) Frontier Kohn-Sham orbitals, (b) 2D plot of laplacian of electron density (red = charge concentration, blue = charge depletion) and (c) electron localization function in the molecular plane.

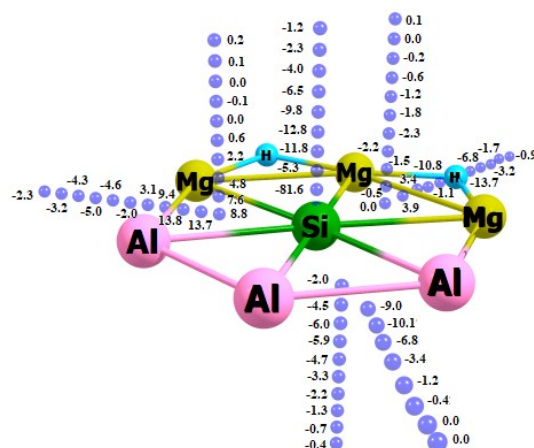


Figure 4. NICS results of $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$ cluster.

We then turned our attention to the lowest energy isomerization pathway between the two lowest energy isomers (Figure 5). For that the probable transition state has been fully optimized at M06-2X/Def2-TZVP level. Harmonic frequency calculation along with the intrinsic reaction coordinate (Figure 4, top) analyses confirm the characterization of the transition state. The calculated barrier at CCSD(T)/Def2-TZVP//M06-2X/Def2-TZVP is 33.8 kcal/mol which is sufficient for the spectroscopic identification of the local minimum structure. The calculated IR spectra is shown in Table S1. Further, the dynamic stability of the cluster has been analyzed using Born-Oppenheimer molecular dynamics (BOMD) simulations at 300K and 400K (Figure 5) for 20 ps duration. The phSi structure is maintained during the simulation over a period of 20 ps.

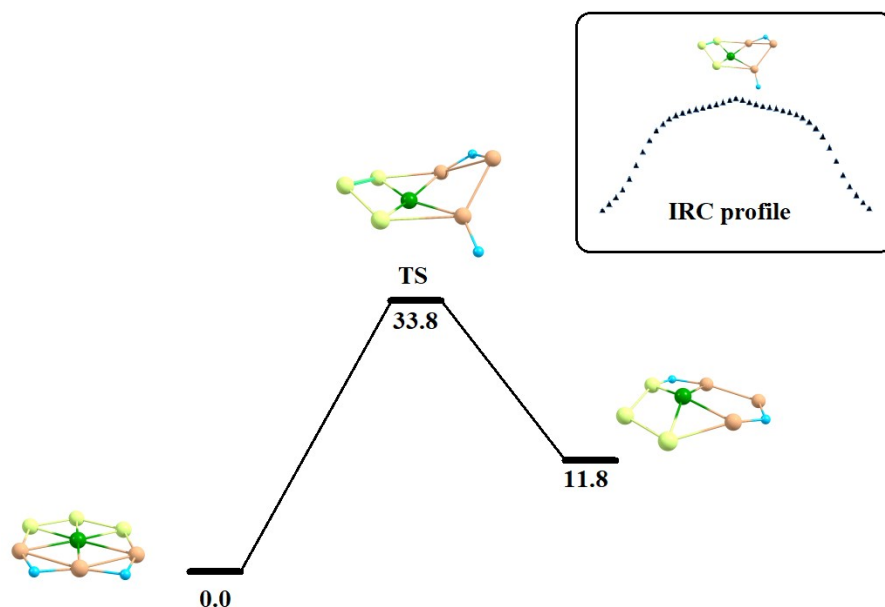


Figure 4. Lowest energy isomerisation pathway between the two lowest energy singlet isomers calculated at CCSD(T)/Def2-TZVP//M06-2X/Def2-TZVP level of theory. The energy values are in kcal/mol. IRC pathway is also shown.

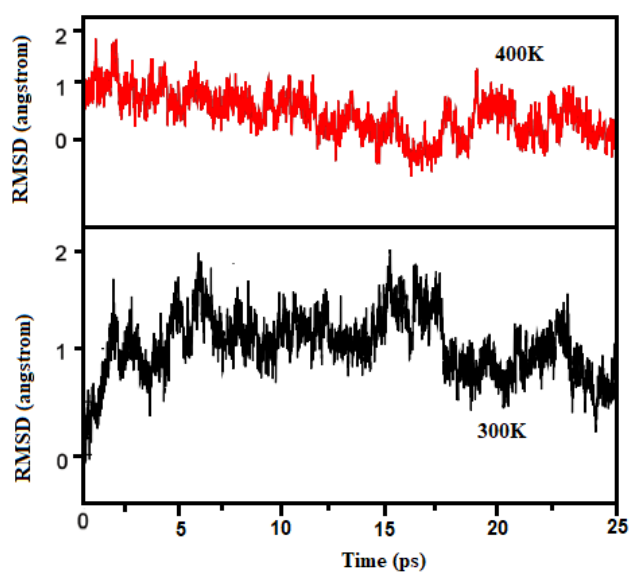


Figure 5. Plots of RMSD (Å) versus time (ps) obtained with BOMD simulations for $\text{SiAl}_5\text{Mg}_3\text{H}_2^+$ cluster at 300 K and 400 K calculated at M06-2X/Def2-TZVP.

Conclusions

In conclusion, a cationic 20-electron $\text{SiAl}_3\text{Mg}_3\text{H}_2^+$ species is designed with a planar hexacoordinate silicon (phB) centre. Bonding analyses of the local minimum structure reveal

partial Si-Al double bond which is a key factor for realization of phSi.³³ NICS calculation reveals that the cyclic delocalization is absent in the cluster. The lowest energy pathway of isomerization to nearest energy isomer involves a sufficiently high barrier, enough for its experimental characterization. The cluster is dynamically stable even at elevated temperature as revealed by BOMD calculations. Similar kinetically stable local minimum structure for hexacoordinate carbon has been reported.^{48,49} Our study reveals the fact that kinetic stability is also an important factor in designing planar hypercoordinate clusters. Owing to the advantage of silicon over carbon in designing 2D architecture, we feel that this study will put impetus in that direction.

Conflicts of interest

Authors declare no conflict of interest.

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