Theoretical Investigation of Hyper-coordinate Planar Si Clusters in [SiM_nH_n]^q
(M = Cu, Ni and n = 4, 5, 6)

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ABSTRACT
In this study, the geometries of the [SiNi_nH_n]^q and [SiCu_nH_n]^q clusters, (n = 4,5,6 and q = 0,+1,-1) complexes have been optimized to form complexes with four, five and six planar and non-planar substituents, with negative, neutral or positive atomic charge, using Density Functional Theory (DFT) at B3LYP/6-311+G (3df, p) computational level and then their thermodynamic stability were investigated by studying the obtained smallest vibrational frequencies and binding energy.

Keywords: Hyper-coordinate; Planar Si; Si Clusters; Density Functional Theory (DFT); Thermodynamic stability

INTRODUCTION
Silicon lies directly under carbon in the same column of the periodic table and has a similar valence orbital configuration (3s^23p^2) with carbon (2s^22p^2). But it almost doubles carbon in sizes. This situation requires a much bigger cavity to geometrically fit a planar coordinate silicon than that to host a planar coordinate carbon. The existence of planar tetra-coordinate silicon (ptSi) cluster with the symmetry of D_{2h} was firstly recognized about 35 years ago in ortho-silicic acid ester [1,2] and C_{2v} ptSi and C_{2v} planar tetra-coordinate germanium (ptGe) cluster were recently observed in penta-atomic MAI_4^- anions and MAI_4 molecule in gas phases (M = Si and Ge) [3,4]. Density Functional Theory (DFT) investigations indicate that the most stable isomer of Si(CO)_4 contains a D_{2h} ptSi center [5-7].

Li’s group proposed a general pattern for planar tetra-, penta-, hexa-, hepta-, and octa-coordinate silicon clusters [8,9]. They also with DFT investigations, indicate that ptSi and ptGe can be stabilized at the centers of the perfectly squared M_4Cl_4 ligands to form D_{4h} M_4Cl_4X complexes (M = Ni, Pd, Pt; X = Si, Ge) [10]. Li’s group also designed planar penta-coordinate silicon (ppSi) cluster in the perfect pentagons of D_{5h} M_5H_5Si (M = Ag, Au, Pd, Pt) [11]. Also they designed the planar hexa-coordinate silicon (phSi) cluster in the perfect hexagon of D_{6h} Cu_6H_6Si [12]. In their work, they continue to present ab initio theoretical evidence of hexa-coordinate planar main group atoms centered in hexagonal hydrocopper complexes Cu_6H_6X (X = Si, P, As). Their results obtained extend the bonding.
capacity of silicon, phosphorus, and arsenic to planar hexa-coordination in hydrometal complexes which are important in fundamental research and may shed new insight into catalyst chemistry. The results obtained in their works complete the series of the much concerned planar coordinate silicon clusters with the highest symmetries of D$_{4h}$, D$_{5h}$, and D$_{6h}$ in M$_n$N$_n$Si complex series (M = transition metals; N = H, Cl; n = 4, 5, 6).

In the present study, we report new quantum chemical calculations for tetra-, penta-, and hexa-coordinate silicon in M$_n$H$_n$Si$^q$ (M=Cu, Ni and n=4, 5, 6) complexes that contain Si centers in a perfect tetra, penta, and hexagonal hydrometals (M$_n$H$_n$) with D$_{nh}$ and C$_{nv}$ symmetries that $q$ is as negative, neutral or positive in these complexes. In the next study, we will use atomic properties, topological specifications of electron density, and respective critical points (CP) for description of bonding in the silicon hydrometal clusters that have utilized for the explanation of plenty of chemical concepts in the bonding realm [13-19].

**METHODS AND COMPUTATIONS**

Here, we use the Density Functional Theory (DFT) with the exchange-correlation potential that constructed from Becke’s three parameter formula for exchange (B3) [20,21] along with the Lee-Yang-Parr parameterization for correlation (LYP) [22]. These calculations were performed within 6-311+G(3df,p) basis set and imaginary frequencies checked at the same theoretical level.

In this study, structures of four, five, and six-coordinate complexes as [SiX$_n$H$_n$]$^q$, if X = Ni, Cu and q = 0, +1, -1, were optimized and then vibrational frequencies and zero-point energies were calculated at the B3LYP/6-311+G(3df,p) level using the optimized geometries and analytical second derivatives. All *ab initio* calculations have been performed using Gaussian 09 software [23].

**RESULTS AND DISCUSSION**

Equilibrium geometries of tetra, penta and hexa hydrometals with Cupper (Cu$_n$H$_n$) and Nickel (Ni$_n$H$_n$) and [SiCu$_n$H$_n$]$^q$ and [SiNi$_n$H$_n$]$^q$ complexes at B3LYP/6-311+G(d,p) quantum computational level are shown in Figures 1-3. The optimized bond lengths R (Å), lowest vibrational frequencies $\nu_{min}$ (cm$^{-1}$), total energy ($\epsilon$), Zero-Point Correction (ZPE) and binding energy ($\Delta E$) of (Cu$_n$H$_n$) and Nickel (Ni$_n$H$_n$) and [SiCu$_n$H$_n$]$^q$ and [SiNi$_n$H$_n$]$^q$ complexes are obtained as listed in Tables 1-3.

According to Table 1, Cu$_4$H$_4$ and Ni$_4$H$_4$ hydrometals with D$_{4h}$ symmetry are local minimum and transition state species respectively. The perfect planar D$_{4h}$ SiCu$_4$H$_4$ cluster and pyramidal C$_{4v}$ SiCu$_4$H$_4$ cluster with Si lying 1.78 Å above the Cu$_4$ plane were confirmed to be forth order saddle point with four imaginary frequencies and second order saddle point with two imaginary frequencies respectively. Also the perfect planar D$_{4h}$ SiNi$_4$H$_4$ cluster and pyramidal C$_{4v}$ SiNi$_4$H$_4$ cluster with Si lying 0.96 Å above the Ni$_4$ plane were confirmed to be transition states with one imaginary frequency and local minimum without imaginary frequency respectively.

Concerning the stability of these structures, we calculated the binding energy ($\Delta E$) of SiM$_4$H$_4$ complex relative to M$_4$H$_4$ hydrometal and free Si atom (as singlet and triplet) with considering zero-point correction ($E=\epsilon+ZPE$). The calculated binding energy ($\Delta E$) for the reaction SiM$_4$H$_4$ → M$_4$H$_4$ + Si clearly demonstrates the stability of the C$_{4v}$ SiM$_4$H$_4$ with respect to dissociation to the hydrometal M$_4$H$_4$ and the free Si atom is...
more than $D_{4h}$. Also the calculated binding energy in $\text{SiM}_4\text{H}_4$ complexes with $M = \text{Ni}$ are much more than $M = \text{Cu}$.

$\text{Cu}_4\text{H}_4 (D_{4h})$  $\text{SiCu}_4\text{H}_4 (D_{4h})$  $\text{SiCu}_4\text{H}_4 (C_{4v})$

$\text{Ni}_4\text{H}_4 (D_{5h})$  $\text{SiNi}_4\text{H}_4 (D_{5h})$  $\text{SiNi}_4\text{H}_4 (C_{5v})$

Fig. 1. Optimized $\text{M}_4\text{H}_4$ hydrometals and $[\text{SiM}_4\text{H}_4]^q$ complexes ($M = \text{Cu, Ni}$ and $q=0$) at B3LYP/6-311+G(3df,p).

$\text{Cu}_5\text{H}_5 (D_{5h})$  $\text{SiCu}_5\text{H}_5 (D_{5h})$  $\text{SiCu}_5\text{H}_5 (C_{5v})$

$\text{Ni}_5\text{H}_5 (D_{5h})$  $\text{SiNi}_5\text{H}_5 (D_{5h})$  $\text{SiNi}_5\text{H}_5 (C_{5v})$  $\text{SiNi}_5\text{H}_5 (D_{5h})$

Fig. 2. Optimized $\text{M}_5\text{H}_5$ hydrometals and $[\text{SiM}_5\text{H}_5]^q$ complexes ($M = \text{Cu, Ni}$ and $q=-1,0,+1$) at B3LYP/6-311+G(3df,p).
Fig. 3. Optimized $M_6H_6$ hydrometals and $[SiM_6H_6]^q$ complexes ($M=\text{Cu, Ni}$ and $q=-1,0,+1$) at B3LYP/6-311+G(3df,p).

Table 1. Optimized bond lengths $R$ (Å), lowest vibrational frequencies $\nu_{\text{min}}$ (cm$^{-1}$), total energy and Zero-Point Energy of $M_4H_4$ hydrometals and $[SiM_4H_4]^q$ complexes ($M=\text{Cu, Ni}$ and $q=0$) and Binding Energy of $[SiM_4H_4]^q$ complexes at B3LYP/6-311+G(3df,p)

<table>
<thead>
<tr>
<th></th>
<th>$Cu_4H_4$</th>
<th>$SiCu_4H_4$</th>
<th>$SiCu_4H_4$</th>
<th>$Ni_4H_4$</th>
<th>$SiNi_4H_4$</th>
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<td>2.437</td>
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<td>-324</td>
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<td>-115</td>
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<td>$\nu_{\text{min}}$ (cm$^{-1}$)</td>
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<td>-152</td>
<td>-324</td>
<td>-105</td>
<td>-115</td>
<td>105</td>
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<tr>
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<td>-6325.12687</td>
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<td>Binding Energy (kcal/mol)</td>
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<td>$S$</td>
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<td>41.649</td>
<td>178.440</td>
<td>183.492</td>
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<td>$T$</td>
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<td>157.692</td>
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<td>Symmetry</td>
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<td>$D_{4h}$</td>
<td>$C_{4v}$</td>
<td>$D_{4h}$</td>
<td>$D_{4h}$</td>
<td>$C_{4v}$</td>
</tr>
</tbody>
</table>

S: Singlet Si; T: Triplet Si; TS: Transition state; 2ed: Second order saddle point; 4th: fourth order saddle point.
Table 2. Optimized bond lengths R (Å), lowest vibrational frequencies $v_{\text{min}}$ (cm$^{-1}$), total energy and Zero-Point Energy of M$_5$H$_5$hydrometals and [SiM$_5$H$_5$]$^q$ complexes (M=Cu, Ni and q = -1, 0, +1) and Binding Energy of [SiM$_5$H$_5$]$^q$ complexes at B3LYP/6-311+G(3df,p)

<table>
<thead>
<tr>
<th></th>
<th>Cu$_5$H$_5$</th>
<th>SiCu$_5$H$_5$</th>
<th>SiCu$_5$H$_5^+$</th>
<th>Ni$_5$H$_5$</th>
<th>Ni$_5$H$_5^+$</th>
<th>SiNi$_5$H$_5^-$</th>
<th>SiNi$_5$H$_5^-$</th>
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<tr>
<td>$R_{M-M}$(Å)</td>
<td>2.490</td>
<td>2.633</td>
<td>2.430</td>
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<td>2.523</td>
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<tr>
<td>$R_{M-H}$(Å)</td>
<td>1.605</td>
<td>1.650</td>
<td>1.647</td>
<td>1.637</td>
<td>1.567, 1.579, 1.583, 1.625, 1.629</td>
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<tr>
<td>$R_{M-Si}$(Å)</td>
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<td>2.237</td>
<td>2.375</td>
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<tr>
<td>$v_{\text{min}}$(cm$^{-1}$)</td>
<td>58.03</td>
<td>58.03</td>
<td>67.62</td>
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<td>E (a.u.)</td>
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<td>7833.7891</td>
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<td>26.558, 27.261, 27.621</td>
<td>26.866</td>
<td>26.866</td>
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Table 3. Optimized bond lengths R (Å), lowest vibrational frequencies $v_{\text{min}}$ (cm$^{-1}$), total energy and Zero-Point Energy of M$_6$H$_6$ hydrometals and [SiM$_6$H$_6$]$^q$ complexes (M=Cu, Ni and q=0) and and Binding Energy of [SiM$_6$H$_6$]$^q$ complexes at B3LYP/6-311+G(3df,p)

<table>
<thead>
<tr>
<th></th>
<th>Cu$_6$H$_6$</th>
<th>SiCu$_6$H$_6$</th>
<th>Ni$_6$H$_6$</th>
<th>SiNi$_6$H$_6$</th>
<th>SiNi$_6$H$_6$</th>
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<tbody>
<tr>
<td>$R_{M-M}$(Å)</td>
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<td>2.443</td>
<td>2.251</td>
<td>2.346</td>
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<tr>
<td>$R_{M-H}$(Å)</td>
<td>1.590</td>
<td>1.600</td>
<td>1.622</td>
<td>2.444</td>
<td>3.088</td>
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<tr>
<td>$R_{M-Si}$(Å)</td>
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<td>40.35</td>
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<td>-238.51</td>
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<tr>
<td>$v_{\text{min}}$(cm$^{-1}$)</td>
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<td>40.35</td>
<td>-344.76</td>
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<tr>
<td>E (a.u.)</td>
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<td>-10136.28588</td>
<td>-9053.19386</td>
<td>-9342.93294</td>
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<td>ZPE (kcal/mol)</td>
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<td>31.140</td>
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<tr>
<td>Binding Energy (kcal/mol)</td>
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<td>74.340</td>
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<td>186.943</td>
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<td>Symmetry</td>
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<td>D$_{3h}$</td>
<td>C$_{5v}$</td>
<td>D$_{5h}$</td>
<td>C$_{5v}$</td>
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</table>

S: Singlet Si; T: Triplet Si; TS: Transition state; 2ed: Second order saddle point; 4th: fourth order saddle point.

The Cu-Cu bond lengths listed in Table 1 show that D$_{4h}$ SiCu$_4$H$_4$ complex is outward contracted compared to the original D$_{4h}$ Cu$_4$H$_4$. This implies that the introduction of X centers destabilize the complex, as substantiated by the minus value binding energy of D$_{4h}$ SiCu$_4$H$_4$ mentioned in Table 1. Contrary C$_{4v}$ SiCu$_4$H$_4$ complex is inward contracted compared to the original D$_{4h}$ Cu$_4$H$_4$. This implies that the introduction of X centers help to stabilize the complex, as substantiated by the considerable binding energy of C$_{4v}$ SiCu$_4$H$_4$. The Ni-Ni bond
lengths listed in Table 1 show that SiNi$_4$H$_4$ complexes is outward contracted compared to the original D$_{4h}$ Ni$_4$H$_4$, but the M-Si bond lengths in M = Ni less than M = Cu show that the binding energy of SiNi$_4$H$_4$ complexes are much more SiCu$_4$H$_4$ complexes.

According to Table 2, the Cu$_5$H$_5$ hydrometal with D$_{5h}$ symmetry is local minimum. Ni$_5$H$_5$ hydrometal is not obtained because it is a radical unstable, therefor Ni$_5$H$_5$ and Ni$_5$H$_5^+$ hydrometals are optimized with D$_{5h}$ symmetry in third order saddle point and with C$_{2v}$ symmetry in second order saddle point. The perfect planar D$_{5h}$ SiCu$_5$H$_5$ cluster and pyramidal C$_{5v}$ SiCu$_5$H$_5$ cluster with Si lying 1.17 Å above the Cu$_5$ plane were confirmed to be transition states and local minimum respectively. Also the perfect planar D$_{5h}$ SiNi$_5$H$_5$ and SiNi$_5$H$_5^+$ clusters were confirmed to be local minimum without imaginary frequency.

The calculated binding energy (\(\Delta E\)) for the reaction SiM$_5$H$_5$ \(\rightarrow\) M$_5$H$_5$ + Si clearly demonstrates the stability of the C$_{5v}$ SiNi$_5$H$_5$ with respect to dissociation to the hydrometal Ni$_5$H$_5$ and the free Si atom is more than D$_{5h}$. Also the calculated binding energy in SiNi$_5$H$_5$ and SiNi$_5$H$_5^+$ complexes are much more than SiCu$_5$H$_5$ complexes.

Although the Cu-Cu and Ni-Ni bond lengths listed in Table 2 show that D$_{5h}$ SiM$_5$H$_5$ complexes are outward contracted compared to the original D$_{5h}$ M$_5$H$_5$, but the M-Si bonds in SiM$_5$H$_5$ complexes than SiNi$_5$H$_4$ and pentagonal shape of complexes are cased to stabilize these complexes, as substantiated by the considerable binding energy.

According to Table 3, Cu$_6$H$_6$ and Ni$_6$H$_6$ hydrometals with D$_{6h}$ symmetry are local minimum and are seventh order saddle point species respectively. Also the perfect planar D$_{6h}$ SiNi$_6$H$_6$ cluster and pyramidal C$_{6v}$ SiNi$_6$H$_6$ cluster with Si lying 0.22 Å above the Ni$_6$ plane were confirmed to be sixth order saddle point with six imaginary frequencies and third order saddle point with three imaginary frequencies respectively. The perfect planar D$_{6h}$ SiCu$_6$H$_6$ cluster was confirmed to be local minimum, contrary to what has been stated by Li [8] that this structure to be transition state. Then Li has been mentioned [8], the energy differences among the C$_{2v}$ pyramid, C$_{6v}$ pyramid, and D$_{6h}$ hexagon of SiCu$_6$H$_6$ are smaller than their differences in zero-point energies. Therefore, the vibrationally averaged structure of SiCu$_6$H$_6$ is actually planar.

The calculated binding energy (\(\Delta E\)) for the reaction SiNi$_6$H$_6$ \(\rightarrow\) M$_6$H$_6$ + Si clearly demonstrates the stability of the C$_{6v}$ SiNi$_6$H$_6$ with respect to dissociation to the hydrometal Ni$_6$H$_6$ and the free Si atom is more than D$_{6h}$. Also the calculated binding energy in SiM$_4$H$_4$ complexes with M = Ni are much more than M = Cu.

Although the Ni-Ni bond lengths listed in Table 3 show that D$_{6h}$ SiNi$_6$H$_6$ complexes are outward contracted compared to the original D$_{6h}$ Ni$_6$H$_6$, but the increasing M-Si bonds in SiM$_6$H$_6$ complexes than SiNi$_6$H$_4$ and SiNi$_5$H$_5$ and hexagonal shape of complexes are cased to stabilize these complexes, as substantiated by the considerable binding energy.

CONCLUSION

We report here the bonding features of the hydrometal complexes D$_{nh}$ and C$_{nv}$ SiM$_n$H$_n$ (n = 4, 5, 6 and M = Cu, Ni). First, the D$_{4h}$ SiCu$_4$H$_4$ complex was obtained unstable, but contrary D$_{4h}$ SiNi$_4$H$_4$ that was obtained as transition state with one imaginary frequency, pyramidal C$_{4v}$ SiNi$_4$H$_4$ was confirmed to be local minimum without imaginary frequency. Second, the perfect planar D$_{5h}$ SiCu$_5$H$_5$ cluster and pyramidal C$_{5v}$ SiCu$_5$H$_5$ cluster were confirmed to be...
transition states and local minimum respectively. Also the perfect planar $D_{5h}$ SiNi$_5$H$_5^-$ and SiNi$_5$H$_5^+$ clusters were confirmed to be local minimum. Third, the perfect planar $D_{6h}$ SiCu$_6$H$_6$ cluster was confirmed to be local minimum, contrary to what has been stated by Li [8] that this structure to be transition state, but the perfect planar $D_{6h}$ SiNi$_6$H$_6$ and pyramidal $C_{6v}$ SiNi$_6$H$_6$ clusters were confirmed to be saddle point.

REFERENCES