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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 ($3s^2 3p^2$) with carbon ($2s^2 2p^2$). 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 MAl_4^- anions and MAl_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-coordiante 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

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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_nN_nSi 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 $M_nH_nSi^q$ (M=Cu, Ni and n=4, 5, 6) complexes that contain Si centers in a perfect tetra, penta, and hexagonal hydrometals (M_nH_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 $[SiX_nH_n]^q$, 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_nH_n) and Nickel (Ni_nH_n) and $[SiCu_nH_n]^q$ and $[SiNi_nH_n]^q$ 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 υ_{min} (cm^{-1}), total energy (ε), Zero-Point Correction (ZPE) and binding energy (ΔE) of (Cu_nH_n) and Nickel (Ni_nH_n) and $[SiCu_nH_n]^q$ and $[SiNi_nH_n]^q$ complexes are obtained as listed in Tables 1-3.

According to Table 1, Cu_4H_4 and Ni_4H_4 hydrometals with D_{4h} symmetry are local minimum and transition state species respectively. The perfect planar D_{4h} $SiCu_4H_4$ cluster and pyramidal C_{4v} $SiCu_4H_4$ 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} $SiNi_4H_4$ cluster and pyramidal C_{4v} $SiNi_4H_4$ 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 (ΔE) of SiM_4H_4 complex relative to M_4H_4 hydrometal and free Si atom (as singlet and triplet) with considering zero-point correction (E= ε + ZPE). The calculated binding energy (ΔE) for the reaction $SiM_4H_4 \rightarrow M_4H_4 + Si$ clearly demonstrates the stability of the C_{4v} SiM_4H_4 with respect to dissociation to the hydrometal M_4H_4 and the free Si atom is more than D_{4h}. Also the calculated binding energy in SiM_4H_4 complexes with M = Ni are much more than M = Cu.

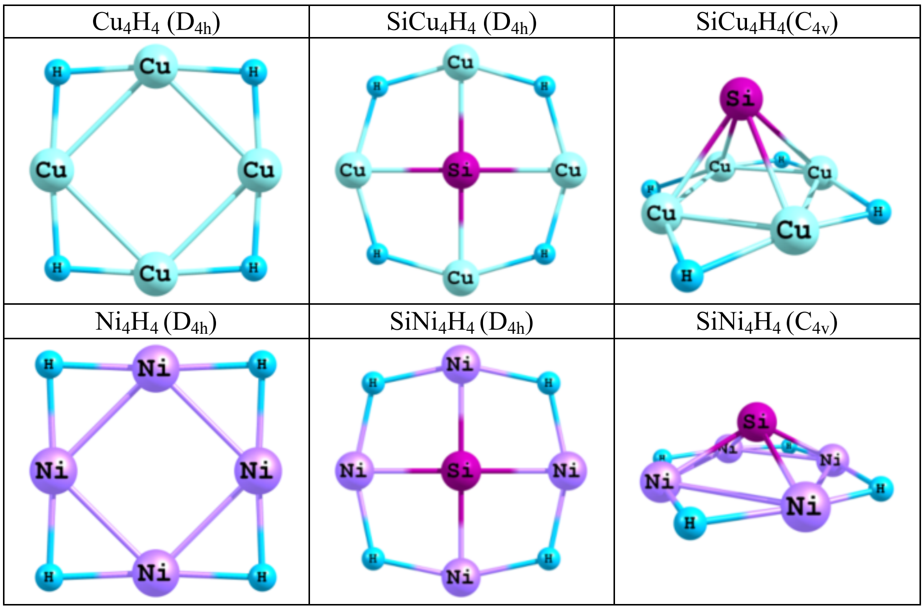

Cu_4H_4 (D_{4h})
$SiCu_4H_4$ (D_{4h})
$SiCu_4H_4$(C_{4v})
Ni_4H_4 (D_{4h})
$SiNi_4H_4$ (D_{4h})
$SiNi_4H_4$ (C_{4v})

Fig. 1. Optimized M_4H_4 hydrometals and $[SiM_4H_4]^q$ complexes (M=Cu, Ni and q=0) at B3LYP/6-311+G(3df,p).

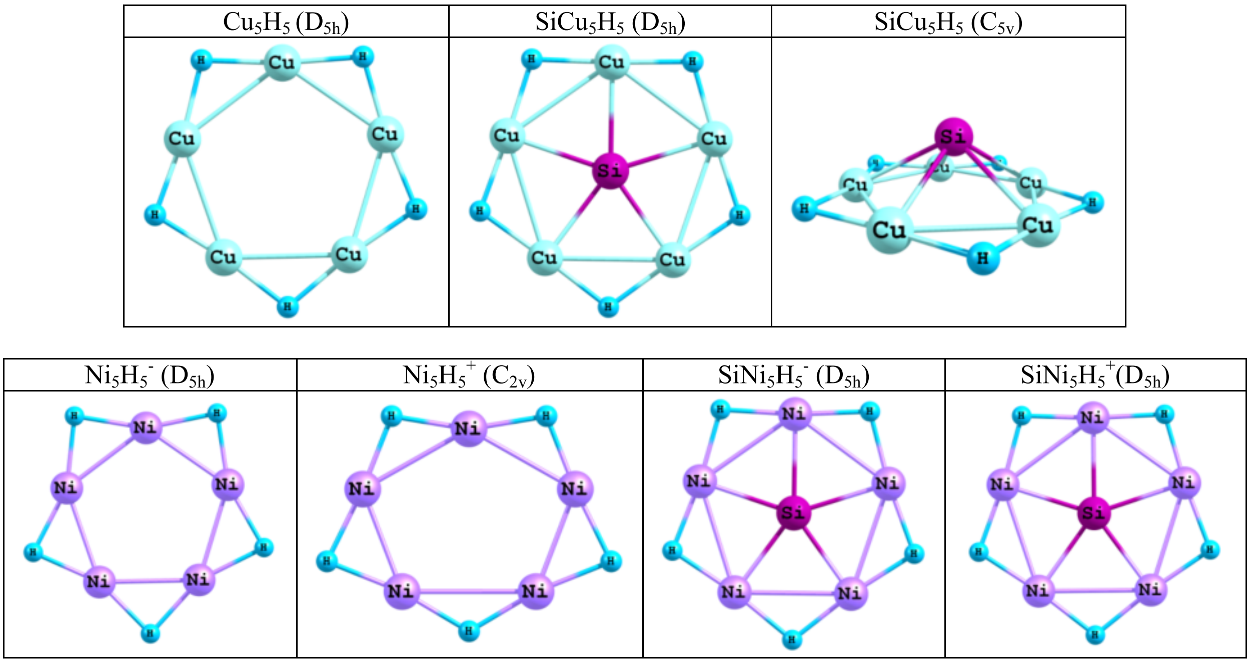
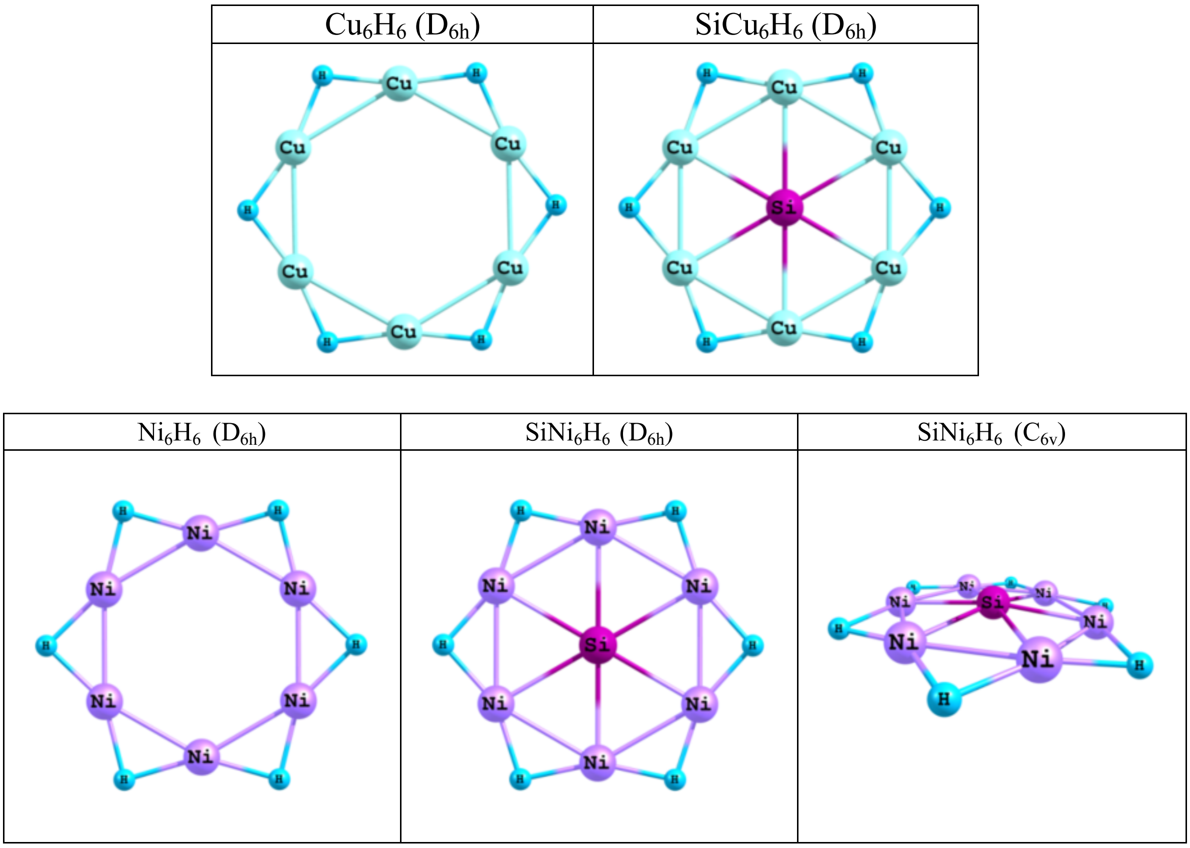

Cu_5H_5 (D_{5h})
$SiCu_5H_5$ (D_{5h})
$SiCu_5H_5$ (C_{5v})
$Ni_5H_5^-$ (D_{5h})
$Ni_5H_5^+$ (C_{2v})
$SiNi_5H_5^-$ (D_{5h})
$SiNi_5H_5^+$(D_{5h})

Fig. 2. Optimized M_5H_5 hydrometals and $[SIM_5H_5]^q$ complexes (M=Cu,Ni and q=-1,0,+1) at B3LYP/6-311+G(3df,p).



Cu_6H_6 (D_{6h}) | $SiCu_6H_6$ (D_{6h})

Ni_6H_6 (D_{6h}) | $SiNi_6H_6$ (D_{6h}) | $SiNi_6H_6$ (C_{6v})

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

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

		Cu_4H_4	**$SiCu_4H_4$**	**$SiCu_4H_4$**	**Ni_4H_4**	**$SiNi_4H_4$**	**$SiNi_4H_4$**
R_{M-M}(Å)		2.437	3.778	2.379	2.381	2.847	2.608
R_{M-H}(Å)		1.635	1.759	1.679	1.620	1.697	1.655
R_{M-Si}(Å)			2.176	2.448		2.013	2.079
υ_{min}(cm^{-1})		73	-152	-324	-105	-115	105
E (a.u.)		-6564.52745	-6853.85434	-6853.94227	-6035.49161	-6325.12687	-6325.13873
ZPE (kcal/mol)		19.615	13.736	16.724	19.835	18.481	20.872
Binding Energy (kcal/mol)	S		-10.539	41.649		178.440	183.492
	T		-36.339	15.850		152.641	157.692
		LM	4th	2ed	TS	TS	LM
Symmetry		D_{4h}	D_{4h}	C_{4v}	D_{4h}	D_{4h}	C_{4v}

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 υ_{min} (cm^{-1}), total energy and Zero-Point Energy of M_5H_5hydrometals and $[SiM_5H_5]^q$ complexes (M=Cu, Ni and q = -1, 0, +1) and Binding Energy of $[SiM_5H_5]^q$ complexes at B3LYP/6-311+G(3df,p)

		Cu_5H_5	**$SiCu_5H_5$**	**$SiCu_5H_5$**	**$Ni_5H_5^-$**	**$Ni_5H_5^+$**	**$SiNi_5H_5^-$**	**$SiNi_5H_5^+$**
R_{M-M}(Å)		2.490	2.633	2.430	2.248	2.212, 2.459, 2.695	2.523	2.522
R_{M-H}(Å)		1.605	1.650	1.647	1.637	1.567, 1.579, 1.583, 1.625, 1.629	1.619	1.608
R_{M-Si}(Å)			2.239	2.375			2.146	2.145
υ_{min}(cm^{-1})		58.03	-128.54	67.62	-50.04	-175.9	73.79	2.71
E (a.u.)		-8205.67565	-8495.10967	-8495.13026	-7544.49632	-7544.16409	-7834.19299	-7833.78914
ZPE (kcal/mol)		25.765	23.813	24.705	23.549	26.558	27.261	26.866
Binding Energy (kcal/mol)	S		52.758	64.786			211.909	170.371
	T		26.959	38.988			186.111	144.572
		LM	TS	LM	3rd	2ed	LM	LM
Symmetry		D_{5h}	D_{5h}	C_{5v}	D_{5h}	C_{2v}	D_{5h}	D_{5h}
S: Singlet Si; T: Triplet Si; TS: Transition state; 2ed: Second order saddle point; 4th: fourth order saddle point.								

Table 3. Optimized bond lengths R (Å), lowest vibrational frequencies υ_{min} (cm^{-1}), total energy and Zero-Point Energy of M_6H_6 hydrometals and $[SiM_6H_6]^q$ complexes (M=Cu, Ni and q=0) and and Binding Energy of $[SiM_6H_6]^q$ complexes at B3LYP/6-311+G(3df,p)

		Cu_6H_6	**$SiCu_6H_6$**	**Ni_6H_6**	**$SiNi_6H_6$**	**$SiNi_6H_6$**
R_{M-M}(Å)		2.546	2.443	2.251	2.346	2.274
R_{M-H}(Å)		1.590	1.600	1.622	1.578	1.650
R_{M-Si}(Å)			2.444		3.088	2.289
υ_{min} (cm^{-1})		21.64	40.35	-344.76	-353.53	-238.51
E (a.u.)		-9846.81402	-10136.28588	-9053.19386	-9342.93294	-9342.88564
ZPE (kcal/mol)		30.929	31.140	30.697	31.056	30.508
Binding Energy (kcal/mol)	S		74.340		241.875	212.742
	T		48.541		216.076	186.943
		LM	LM	7th	6th	3th
Symmetry		D_{6h}	D_{6h}	D_6h	D_6h	C_{6v}
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} $SiCu_4H_4$ complex is outward contracted compared to the original D_{4h} Cu_4H_4. This implies that the introduction of X centers destabilize the complex, as substantiated by the minus value binding energy of D_{4h} $SiCu_4H_4$ mentioned in Table 1. Contrary C_{4v} $SiCu_4H_4$ complex is inward contracted compared to the original D_{4h} Cu_4H_4. This implies that the introduction of X centers help to stabilize the complex, as substantiated by the considerable binding energy of C_{4v} $SiCu_4H_4$. The Ni-Ni bond lengths listed in Table 1 show that $SiNi_4H_4$ complexes is outward contracted compared to the original D_{4h} Ni_4H_4, but the M-Si bond lengths in M = Ni less than M = Cu show that the binding energy of $SiNi_4H_4$ complexes are much more $SiCu_4H_4$ complexes.

According to Table 2, the Cu_5H_5 hydrometal with D_{5h} symmetry is local minimum. Ni_5H_5 hydrometal is not obtained because it is a radical unstable, therefor $Ni_5H_5^-$ and $Ni_5H_5^+$ 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} $SiCu_4H_4$ cluster and pyramidal C_{5v} $SiCu_4H_4$ cluster with Si lying 1.17 Å above the Cu_4 plane were confirmed to be transition states and local minimum respectively. Also the perfect planar D_{5h} $SiNi_5H_5^-$ and $SiNi_5H_5^+$ clusters were confirmed to be local minimum without imaginary frequency.

The calculated binding energy (ΔE) for the reaction $SiM_5H_5 \rightarrow M_5H_5 + Si$ clearly demonstrates the stability of the C_{5v} $SiCu_5H_5$ with respect to dissociation to the hydrometal Cu_5H_5 and the free Si atom is more than D_{5h}. Also the calculated binding energy in $SiNi_5H_5^-$ and $SiNi_5H_5^+$ complexes are much more than $SiCu_5H_5$ complexes.

Although the Cu-Cu and Ni-Ni bond lengths listed in Table 2 show that D_{5h} $SiM_5H_5^q$ complexes are outward contracted compared to the original D_{5h} M_5H_5, but the M-Si bonds in SiM_5H_5 complexes than $SiNi_4H_4$ and pentagonal shape of complexes are cased to stabilize these complexes, as substantiated by the considerable binding energy.

According to Table 3, Cu_6H_6 and Ni_6H_6 hydrometals with D_{6h} symmetry are local minimum and are seventh order saddle point species respectively. Also the perfect planar D_{6h} $SiNi_6H_6$ cluster and pyramidal C_{6v} $SiNi_6H_6$ 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} $SiCu_6H_6$ 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 $SiCu_6H_6$ are smaller than their differences in zero-point energies. Therefore, the vibrationally averaged structure of $SiCu_6H_6$ is actually planar.

The calculated binding energy (ΔE) for the reaction $SiNi_6H_6 \rightarrow M_6H_6 + Si$ clearly demonstrates the stability of the C_{6v} $SiNi_6H_6$ with respect to dissociation to the hydrometal Ni_6H_6 and the free Si atom is more than D_{6h}. Also the calculated binding energy in SiM_4H_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} $SiNi_6H_6$ complexes are outward contracted compared to the original D_{6h} Ni_6H_6, but the increasing M-Si bonds in SiM_6H_6 complexes than $SiNi_4H_4$ and $SiNi_5H_5$ 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_nH_n (n = 4, 5, 6 and M = Cu, Ni). First, the D_{4h} $SiCu_4H_4$ complex was obtained unstable, but contrary D_{4h} $SiNi_4H_4$ that was obtained as transition state with one imaginary frequency, pyramidal C_{4v} $SiNi_4H_4$ was confirmed to be local minimum without imaginary frequency. Second, the perfect planar D_{5h} $SiCu_5H_5$ cluster and pyramidal C_{5v} $SiCu_5H_5$ cluster were confirmed to be transition states and local minimum respectively. Also the perfect planar D_{5h} $SiNi_5H_5^-$ and $SiNi_5H_5^+$ clusters were confirmed to be local minimum. Third, the perfect planar D_{6h} $SiCu_6H_6$ 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} $SiNi_6H_6$ and pyramidal C_{6v} $SiNi_6H_6$ clusters were confirmed to be saddle point.

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