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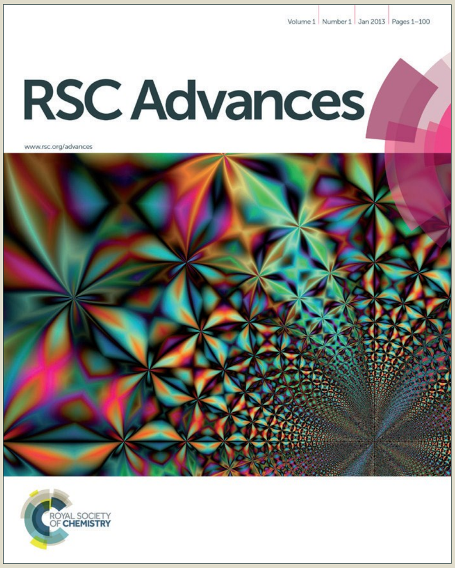

ROYAL SOCIETY OF CHEMISTRY

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# Closoborate-transition metal complexes for hydrogen storage

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## Abstract

We report hydrogen uptake capacity of early transition metal (TM) atom (Sc, Ti and V) decorated closoborate ($B_6H_6$) using density functional theory and second order Møller–Plesset method. Maximum of four hydrogen molecules can be adsorbed on $B_6H_6Sc$, $B_6H_6Ti$ and $B_6H_6V$ complex with their gravimetric hydrogen uptake of 6.51, 6.36, 6.21 wt % respectively. We have used M06, B3LYP and MP2 methods with 6-311++G** basis set for the study. The Gibbs free energy corrected adsorption energies show that adsorption of four $H_2$ molecules on $B_6H_6Ti$ and $B_6H_6V$ is energetically favorable whereas it is unfavorable on $B_6H_6Sc$ at 298.15 K at M06/6-311++G** and B3LYP/6-311++G** level. Many-body analysis approach has been used here to study the nature of interaction between adsorbed $H_2$ molecules and the substrate and that between hydrogen molecules in a complex. The binding energy of $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex is found to be 39.44, 58.43 and 51.03 kcal/mol respectively using M06/6-311++G** level of theory. Interaction between inorganic material-metal complexes with adsorbed $H_2$ molecules is found to be attractive for all the three complexes. The charge transfer between Ti and adsorbed $H_2$ molecules is more than that for Sc and V. The HOMO-LUMO gap shows that all the three $H_2$ adsorbed complexes are kinetically stable. The dimers of TM-closoborate complexes in head-to-tail type configuration and multi-transition metal atom decorated closoborate complexes have also been studied. In both the cases number of $H_2$ molecules adsorbed per TM atom is not affected neither by dimerization nor multi-transition metal atom decoration.

**Keyword :** $H_2$ adsorption, closoborate, many-body analysis, molecular interaction, desorption temperature

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## 1. Introduction

Due to deploying fossil fuels and increasing environmental issues such as global warming it has become necessary to search for a clean and more efficient energy source, its storage options and conversion technologies. Hydrogen is the most abundant element in the universe. It is also the most promising alternative to the carbon based fuels like gasoline. There are no emissions when it is used as an energy carrier. When used in fuel cells it gives water as the only byproduct. It is a light weight and ideal as a synthetic fuel. For using hydrogen as an energy carrier its production is not a problem but its storage in compact and lightweight package is a challenging task. For hydrogen economy to be a reality searching a material capable of storing hydrogen efficiently for vehicular applications is essential. However it is one of the most difficult challenges. As compared to bulk material nanoscale material and small molecules offer a higher energy storage capacity due to their unique properties such as high surface area, size confinement effect etc. [1-4]

Several small organometallic complexes have been considered earlier from hydrogen point of view. It includes transition metal (TM)-acetylene[5-9], TM-ethylene[8,10-20], TM-$C_nH_n$ rings and TM-$C_nH_m$ [21-30] complexes. There are several investigations on large inorganic structures as well for hydrogen storage in the form of hydrides. However hydrides require more energy to release hydrogen as it is stored in atomic form. In order to have the fast adsorption and desorption kinetics hydrogen should be stored in a molecular form. As compared to small organometallic complexes, inorganic material-metal (IOM) complexes have received fewer attentions as a hydrogen storage media. Few efforts are made earlier to study IOM complexes from hydrogen storage point of view.[31-40]

Hydrogen adsorption in $B_6H_2Li_2$ has been studied by Srinivasu et. al. [31] and Pathak et. al.[32] They reported $B_6H_2Li_2$ as a neutral system. In 1964 Boone has prepared the $B_6H_6$ ion which is the smallest member of hydroclosoborate family.[41] Chang et. al. have investigated the atomistic mechanisms governing hydrogen release and uptake processes in ammonia borane using the density functional theory (DFT) method.[33] The spin-polarized DFT has been used to perform the simulations on 3*d* transition metal doped borazine.[34] Hydrogen storage capacity of alkali metal, alkaline-earth metal and Ti decorated borazine has been investigated using DFT by Li et. al.[35] They concluded that the alkali metals bound strongly to the borazine. The $H_2$ uptake capacity of 10.4 wt% was obtained for the Li decorated borazine. Using DFT and Møller–Plesset perturbation theory Pathak et. al. have studied the hydrogen uptake of Li and Mg doped boranes.[36] Structures and binding energies of hydrogen molecules adsorbed structures were calculated.

Hydrogen storage capacity of $Li_mB_6H_6$ (m=1, 2) has been studied by Lu et. al. using DFT and observed that the Li atom bound strongly to the substrate.[37] Bandaru et. al. have constructed the potential energy surface for the $H_2$ release from ammonia borane with a novel bifunctional cationic ruthenium catalyst based on the sterically bulky β-diketiminato ligand using the DFT.[38] Khan and Khan have performed the DFT calculations using hybrid B3PW91 functional to investigate hydrogen storage capacity of Ti, Cr, and Fe doped borazine.[39] They concluded that the hydrogen storage capability of Ti-$B_3N_3H_6$ in its quintet state is half than the triplet state and the quintet state is unfavourable for the hydrogen storage. Samolia and Kumar have studied the hydrogen trapping efficiency of a metal functionalized BN system at various high electron density sites using DFT at M05-2X/6-311G+(d) level of theory.[40] Zhang et. al. have studied Ti substituted boranes computationally for hydrogen storage applications.[42] They predicted the hydrogen storage capacity of $B_5H_5Ti$ and its TiH substituted analogue $B_4H_4Ti_2H_2$ as 8.6 and 10 wt% respectively with respective molecular hydrogen binding energy as -23.5 and -35 kJ/mol per $H_2$ molecule. Kumar et. al. have modified the metal organic framework by incorporating transition metal through –OH and –SH functionalization of triphenyl linkers to improve the hydrogen storage capacity of metal organic framework.[43] They applied atoms in molecules theory to characterize the nature of interaction between $H_2$ and metal centres. Their calculated interaction energy value per $H_2$ varies from -5.47 to -15.67 kcal/mol and is suitable for room temperature hydrogen storage.

Most of the studies on hydrogen storage capacity of IOM complexes have been carried out either with alkali metal or alkaline earth metal doped inorganic material. However it has been observed that hydrogen adsorption on alkali or alkaline earth metal doped organic substrate is energetically unfavorable and these materials are not suitable as hydrogen storage media.[7,9] This is true for wide range of temperature - room temperature, below as well as above room temperature. On the other hand early TM doped systems are good options for hydrogen storage. Therefore we have studied here hydrogen storage capacity of early TM doped inorganic material.

The aim of this work is to study hydrogen adsorption on TM-closoborate (TM= Sc, Ti and V) complexes using DFT and wave function method. The TM-closoborates considered here are $B_6H_6Sc$, $B_6H_6Ti$ and $B_6H_6V$. Using Gibbs free energy corrected hydrogen adsorption energies we have suggested a temperature range over which $H_2$ adsorption is possible on these complexes. Furthermore, the interaction energies between hydrogen molecules and IOM complexes as well as that between different hydrogen molecules in a complex are also studied.

## 2. Computational details

The geometry optimization of $TMB_6H_6(nH_2)$ (TM= Sc, Ti and V) complexes have been carried out using DFT with Becke's three parameter hybrid functional with LYP correlation functional (B3LYP) [44-46], hybrid functional of Truhlar and Zhao(M06) [47] and second order Møller–Plesset (MP2) method.[48] We have used 6-311++G** basis set for all the calculations. All calculations were performed using *Gaussian* 09 suit of programs.[49] Vibrational frequencies are also obtained at the same level of theory. Many-body analysis technique has been used to study nature of interaction between different molecules in hydrogen adsorbed complexes and contribution from many-body energies to the binding energy of a respective complex. [50-53]

### Many-body interaction energies

The decomposition of total energy of a complex can be written as

$$\Delta E = E(12345) - \{E_{IOM} + uE_{H2}\}$$

$$= \sum_{i=1}^{5} E(i) - \{E_{IOM} + uE_{H2}\} \qquad \text{(relaxation energy)}$$

$$+ \sum_{i=1}^{4}\sum_{j>i}^{5} \Delta^2 E_c(ij) \qquad \text{(two-body energy)} \qquad (1)$$

$$+ \sum_{i=1}^{3}\sum_{j>i}^{4}\sum_{k>j}^{5} \Delta^3 E_c(ijk) \qquad \text{(three-body energy)}$$

$$+ \sum_{i=1}^{2}\sum_{j>i}^{3}\sum_{k>j}^{4}\sum_{l>k}^{5} \Delta^4 E_c(ijkl) \qquad \text{(four-body energy)}$$

$$+ \Delta^5 E_c(ijklm) \qquad \text{(five-body energy)}$$

where $E(i)$, $E(ij)$, $E(ijk)$, $E(ijkl)$ and $E(ijklm)$ are the energies of various monomers, dimers, trimers, tetramers and pentamers respectively in a complex. $E_{IOM}$ and $E_{H2}$ are the energies of isolated IOM compound and hydrogen molecule respectively. Here $u$ is the number of hydrogen molecules adsorbed in a complex. The pair wise basis set superposition error (BSSE) corrected two-body interaction energies and higher three-body, four-body, etc. interaction energies are defined as:

$$\Delta^2 E_C(ij) = E(ij) - \{E(i) + E(j)\} \tag{2}$$

$$\Delta^3 E_C(ijk) = E(ijk) - \{E(i) + E(j) + E(k)\} - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\} \tag{3}$$

$$\Delta^4 E_C(ijkl) = E(ijkl) - \{E(i) + E(j) + E(k) + E(l)\} - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(il) + \Delta^2 E(jk) + \Delta^2 E(jl) + \Delta^2 E(kl)\} - \{\Delta^3 E(ijk) + \Delta^3 E(ijl) + \Delta^3 E(ikl) + \Delta^3 E(jkl)\} \tag{4}$$

and so on.

Sum of relaxation energy, two-body energy, three-body energy, four-body energy, and five-body energy gives the binding energy of a complex. The BSSE corrected total energy can be calculated as suggested by Valiron and Mayer [54].

## 3. Results and discussions

We have first optimized the geometries of $B_6H_6M$ (M= Sc, Ti, V) complexes. The $B_6H_6M$ structure has six radially bonded H atoms attached to the B atoms at the vertices of an octahedron. The TM atoms Sc, Ti, V are counter-positioned on top of the face centered sites. Optimized structures of $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ at M06/6-311++G** level of theory are shown in Fig. 1. Maximum of four $H_2$ molecules are adsorbed on $B_6H_6Sc$, $B_6H_6Ti$

and $B_6H_6V$ complex thereby showing their $H_2$ uptake capacity of 6.51, 6.36, 6.21 wt % respectively. It is little higher than the target set by U. S. Department of Energy by 2015 (5.5 wt %). Structural parameters of $H_2$ adsorbed complexes are presented in Table 1. The bond between $B_6H_6$ and transition metal gets little elongated upon $H_2$ adsorption for all the three cases. The elongation is more for $B_6H_6V$ complex than $B_6H_6Sc$ and $B_6H_6Ti$. Hydrogen molecules are adsorbed at shorter distance in $B_6H_6V(4H_2)$ than $B_6H_6Sc(4H_2)$ and $B_6H_6Ti(4H_2)$ complexes.

Not only bond between $B_6H_6$ and transition metal but the H-H bond lengths of $H_2$ molecules also get changed upon adsorption. The calculated H-H bond length for the isolated $H_2$ molecule is found to be 0.750 Å at M06/6-311++G** level of theory. In $B_6H_6Sc(4H_2)$, B6H6Ti($4H_2$) and $B_6H_6V(4H_2)$ complexes the H-H bond lengths are in a range of 0.769-0.786 Å, 0.785-0.824 Å and 0.782-0.821 Å respectively. These H-H bond lengths are longer in $H_2$ adsorbed complexes than that of free $H_2$ molecule. It indicates that there is a Kubas interaction between transition metal atom and adsorbed $H_2$ molecules.[43] This elongation in H-H bond length than the free $H_2$ molecule is due to the charge transfer from *d* orbital of the transition metal atom to the adsorbed $H_2$ molecules.

Thermodynamic calculations have been carried out to evaluate the averaged $H_2$ adsorption energy. The averaged adsorption energy with Gibbs free energy correction $\Delta E_G$) for 'n' number of $H_2$ adsorbed TM:$B_6H_6$ complex is calculated as :

$$\Delta E_G = \{E_G[IOM] + n\, E_G[H_2] - E_G[IOM(H_2)_n]\}/n$$

Here $E_G[X]$ stands for the total energy of a complex $X$ with Gibbs free energy correction.

$E_G\,[X]$ and Gibbs free energy correction $E_{Gcorr}[X]$ are given by :

$$E_G[X] = E[X] + E_{Gcorr}[X], \text{ and}$$

$$E_{Gcorr}[X] = E_{zpe}[X] + E_{thm}[X] + k_B T - T\,S[X]$$

Here $E[X]$ is the total energy of a complex $X$, $E_{zpe}[X]$ is the zero-point energy, $E_{thm}[X]$ is the energy due to sum of translational, rotational and vibrational motion of $X$, $k_B$ is the Boltzmann's constant, and $S[X]$ is the sum of entropy for translational, rotational and vibrational motion of $X$.

Table 2 gives averaged adsorption energies without zero point energy correction ($\Delta E$), with zero point energy correction ($\Delta E_{zpe}$) and with Gibbs free energy correction ($\Delta E_G$) at 298.15 K for $B_6H_6M(4H_2)$ (M = Sc, Ti, V) complexes at M06/6-311++G**, B3LYP/6-311++G** and MP2/6-311++G** levels. The Gibbs free energy corrected adsorption energies show that adsorption of four $H_2$ molecules on $B_6H_6Ti$ and $B_6H_6V$ is energetically favorable whereas it is unfavorable on $B_6H_6Sc$ at 298.15 K using M06 and B3LYP methods. Using MP2 method the adsorption of four $H_2$ molecules on $B_6H_6Sc$ and $B_6H_6V$ complex is thermodynamically unfavorable where as it is favorable for $B_6H_6Ti$ complex at room temperature. In order to find a temperature range over which $H_2$ adsorption on these three complexes is energetically favorable, we have calculated Gibbs free energy corrected $H_2$ adsorption energies for different temperatures. Temperature dependent $\Delta E_G$ values are plotted in Fig. 2 using M06/6-311++G** and B3LYP/6-311++G** levels. As can be seen from Fig. 2 adsorption of four $H_2$ molecules on $B_6H_6Ti$ and $B_6H_6V$ is energetically favorable for all the temperatures considered here at M06/6-311++G** as well as B3LYP/6-311++G** level of theory. Adsorption of four $H_2$ molecules on $B_6H_6Sc$ is energetically favorable below 270 K and 160 K at M06/6-311++G** and B3LYP/6-311++G** level respectively.

For ideal hydrogen storage the $H_2$ desorption from host material is necessary at ambient conditions. The $H_2$ desorption temperature from $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complexes is obtained using $\Delta E_{ZPE}$ and the Van't Hoff equation[55] as

$$T_D = ( \Delta E_{ZPE} / k_B ) ( \Delta S / R - \ln P )^{-1}$$

where $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23}$ $JK^{-1}$), R the gas constant (8.31 $JK^{-1}$ $Mol^{-1}$), ΔS the change in the $H_2$ entropy from gas to liquid phase and P the equilibrium pressure P (1 atm). Using ΔS from Ref. [56] and values of $\Delta E_{ZPE}$ calculated at M06/6-311++G** level of theory from Table 2, minimum and maximum $H_2$ desorption temperatures ($T_D$) from the $H_2$ adsorbed complexes are calculated. Minimum $H_2$ desorption temperature for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$, $B_6H_6V(4H_2)$ is found to be 332 K, 574 K and 472 K respectively whereas maximum desorption temperature for the respective complexes is 650 K, 1288 K and 956 K using M06/6-311++G** level of theory. The maximum desorption temperatures ($T_D$Max) or the temperatures to desorb all the adsorbed $H_2$ molecules from the host material are calculated using $\Delta E_{ZPE}$ values of the $B_6H_6Sc(1H_2)$, $B_6H_6Ti(1H_2)$ and $B_6H_6V(1H_2)$ complexes. It is found that the maximum desorption temperature is higher for $B_6H_6Ti(4H_2)$ complex relative to other two complexes. This is because when the first $H_2$ molecule is adsorbed on $B_6H_6Ti$ complex more charge get transferred from Ti to the only adsorbed $H_2$ molecule and due to the Kubas interaction the H-H bond length gets more elongated. As the H-H bond length increases corresponding $\Delta E_{ZPE}$ also increases and as a consequence desorption temperature increases as well. Desorption temperatures using other two methods are also given in Table 3. The value for maximum desorption of $B_6H_6V(4H_2)$ complex is not given because its $\Delta E_{ZPE}$ value is found to be negative.

Kinetic stability of $H_2$ adsorbed complexes is verified by using a gap between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) at M06/6-311++G**, B3LYP/6-311++G** and MP2/6-311++G** levels. The HOMO-LUMO gap is plotted for different $H_2$ adsorbed complexes in Fig. 3 at all three the levels of theories used here. The HOMO-LUMO gap for the maximum $H_2$ adsorbed $B_6H_6Sc$ and $B_6H_6Ti$ complexes are higher than that for the respective isolated complexes (before $H_2$ adsorption). It indicates more kinetic stability of $H_2$ adsorbed $B_6H_6Sc$ and $B_6H_6Ti$ complexes than respective isolated IOM complex. There is negligible change in HOMO-LUMO gap for isolated $B_6H_6V$ after maximum $H_2$ adsorption on it. The stability of $H_2$ adsorbed complexes is also verified by calculating vibrational frequencies for the three complexes. Table 4 shows selected vibrational frequencies and their assignment for $H_2$ adsorbed complexes using M06 and B3LYP method. There are no imaginary frequencies for all the three complexes studied indicating that these complexes are quantum mechanically stable.

**Interaction energies between molecules**

Many-body analysis technique has been used here to calculate various interaction energies for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complexes and are presented in Table 5 at M06/6-311++G** level. The % contribution from many-body energies, additive energy and nonadditive energy to the binding energy of $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complexes is shown in Fig. 4, Fig. 5 and Fig. 6 respectively at all the three levels of theories used here. As can be seen from Table 4 total two-body energy has major contribution to the binding energy of a respective $H_2$ adsorbed complex. The binding energy of $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex is found to be 39.44, 58.43 and 51.03 kcal/mol respectively at M06/6-311++G** level. This shows that each hydrogen molecule binds to the transition metal atom with energy in a range of 9.86 to 14.6 kcal/mol at M06/6-311++G** level of theory. It indicates that the complex considered here are suitable for hydrogen storage. The adsorption energies are within the range of physisorption and chemisorption and we expect fast adsorption and desorption kinetics.

Interaction of IOM complex with adsorbed $H_2$ molecules is found to be attractive for all the three complexes. Total attractive contribution from IOM-$H_i$ two-body interactions to the total two-body interaction energy is 103.8, 110.6 and 116.2% for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex respectively. Total repulsive contribution from $H_i$-$H_j$ interaction two-body energy terms to the binding energy of a respective complex is 3.8, 10.6 and 16.2%. As we go from $B_6H_6Sc$ to $B_6H_6V$ attractive % contribution from IOM-$H_i$ terms and repulsive % contribution from $H_i$-$H_j$ terms to the respective total two body energy increases. Though IOM-$H_i$ two-body interaction energies are higher than $H_i$-$H_j$ interaction energies the latter are not negligible.

Contribution from total three body energy to the binding energy of $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ is found to be 19.85 (repulsive), 11.22 (repulsive) and 28.31 (attractive) % respectively. Three-body energies for which IOM is one of the three body terms contribute about 100.8 (repulsive), 117.9 (repulsive) and 91 (attractive) % to total three body energy for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex respectively. Contribution from $H_i$-$H_j$-$H_k$ attractive interaction energy to total three-body energy for the $B_6H_6Sc(4H_2)$ complex is negligible (0.8%) whereas its contribution is 17.9 (attractive) and 9 (attractive) % for the $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex respectively. Most of the IOM-$H_i$-$H_j$ three-body energies are repulsive in nature except the IOM-$H_3$-$H_4$ for $B_6H_6Ti(4H_2)$ and IOM-$H_1$-$H_2$, IOM-$H_1$-$H_3$, IOM-$H_1$-$H_4$, IOM-$H_2$-$H_3$ and IOM-$H_3$-$H_4$ for $B_6H_6V(4H_2)$ which are attractive in nature.

Similar to total two-body and total three-body energy, total four-body and total five-body energies also contribute significantly to the binding energy of respective complex. Total four-body energy has attractive contribution of 14.98, 5.47 and 7.34 % to the binding energy of $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex respectively. Total five body energy contributes repulsively to the binding energy of respective complex and it is about 3.9, 1.8 and 4.9 % for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex respectively. In case of four-body energy the contribution from the four-body energy terms $H_i$-$H_j$-$H_k$-$H_l$ is negligible as compared to IOM- $H_i$-$H_j$-$H_k$ four-body energy terms. The % of contribution from terms containing IOM as one of the four-body terms is 99.3, 98.4 and 99.5 % for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex respectively.

Contribution from the relaxation energy to binding energy of respective complex is also not negligible. It has repulsive contribution of 2.1, 10.7 and 18.9 % for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$ and $B_6H_6V(4H_2)$ complex respectively at M06/6-311++G** level. Its contribution increases from $B_6H_6Sc$ to $B_6H_6V$.

**NBO Analysis:**

Natural bond orbital (NBO) [57] charges are calculated for all the complexes to understand their charge distribution during successive addition of $H_2$ molecules. To get qualitative picture about charge transfer we calculated the charge on Sc, Ti, V atoms in $B_6H_6Sc$, $B_6H_6Ti$, $B_6H_6V$ complexes with successive addition of $H_2$ molecules using the NBO analysis. The charge on TM atom with successive addition of $H_2$ molecules is plotted in Fig. 7 at M06/6-311++G** level. Charge on Sc and V atom is positive before $H_2$ adsorption and remains positive even after adsorption of maximum four $H_2$ molecules on $B_6H_6Sc$ and $B_6H_6V$ complex. Charge on Ti atom is also positive before adsorption of first $H_2$ molecule on $B_6H_6Ti$ and becomes negative after adsorption of four $H_2$ molecules on it. It is observed that charge on Sc before first $H_2$ adsorption is 1.07 and decreases with successive addition of $H_2$ molecule upto third $H_2$ molecule at M06/6-311++G** level. It slightly increases after addition of fourth $H_2$ molecule. A large change in charge on Ti is observed after $H_2$ adsorption. Charge on Ti before first $H_2$ adsorption is

0.91 which becomes -0.54 after fourth $H_2$ molecule adsorption. The charge on V decreases from 1.06 to 0.18 after adsorption of four $H_2$ molecules. Charge transfer is more between Ti and adsorbed $H_2$ molecules than that between Sc and $H_2$ as well as V and $H_2$. This is due to the fact that the Ti atom interacts strongly with the adsorbed $H_2$ molecules than the Sc and V as can be seen from the higher two-body IOM-$H_i$ interaction energies for $B_6H_6Ti(4H_2)$ system than that for $B_6H_6Sc(4H_2)$ and $B_6H_6V(4H_2)$ systems. More the charge transfer between transition metal atom and $H_2$, more is the elongation in the H-H bond lengths. This is confirmed from more elongation in H-H bond lengths for adsorbed $H_2$ molecules in $B_6H_6Ti(4H_2)$ complex than the $B_6H_6Sc(4H_2)$ and $B_6H_6V(4H_2)$ complexes.

### Dimerization of closoborate-TM complex and multi-TM decorated closoborate complexes

We have studied the dimers of closoborate-TM complexes to check whether there is a clustering of transition metal atoms. We have considered here head-to-tail type of dimers and the optimized geometries of one of the three dimers before and after $H_2$ adsorption are shown in Fig. 8. As can be seen from Fig. 8 there is no clustering of transition metal atoms in case of head-to-tail type of structures for all the three cases before as well as after $H_2$ adsorption. The number of $H_2$ molecules adsorbed per TM atom remains four for all the three systems. However $H_2$ molecules adsorbed on sandwiched TM atom are at little longer distance than that on TM atom which is decorated at one end.

We have also investigated multi-transition metal atom-closoborate complexes and their hydrogen storage capacity. Four transition metal atoms are decorated on closoborate for all the three cases. When four TM atoms are decorated on closoborate we do observed clustering of TM atoms. Figure 9 shows one of the three structures with decoration of four Sc atoms on closoborate before and after $H_2$ adsorption. Two pairs of transition metal atom dimers are formed in each case. The Sc-Sc, Ti-Ti and V-V atoms before (after) $H_2$ adsorption are at a distance of 3.034 (3.154), 2.273 (3.069), 1.871 (2.936) Å from each other respectively in each pair. It indicates that TM-TM bond gets elongated upon $H_2$ adsorption. Two pairs of Sc-Sc, Ti-Ti and V-V dimers are at a distance of 5.163, 4.880 and 4.528 respectively from each other in $H_2$ adsorbed complexes. In single TM decorated closoborates, four $H_2$ molecules are adsorbed per TM atom. Clustering of TM atoms does not affect the number of adsorbed $H_2$ molecules per TM atom for all the three cases. Total number of $H_2$ adsorbed on four TM atoms decorated closoborate is sixteen (four $H_2$ per TM atom) for all the three cases. However two of the sixteen $H_2$ molecules are dissociated and adsorbed in atomic form one on each TM dimer as shown in Fig. 9. Each TM dimer adsorbs eight $H_2$ molecules one of which is dissociated.

The averaged $H_2$ adsorption energies for $B_6H_6Sc_4(16H_2)$, $B_6H_6Ti_4(16H_2)$ and $B_6H_6V_4(16H_2)$ complexes without(with) zero point energy correction are found to be 0.52(0.36), 0.59(0.40) and 0.36(0.17) eV respectively. Similar to single TM atom decorated $B_6H_6$ complexes these energies are within the range of physisorption and chemisorption and we expect fast adsorption and desorption kinetics. The Gibbs free energy corrected adsorption energies for $B_6H_6Sc_4(16H_2)$, $B_6H_6Ti_4(16H_2)$ and $B_6H_6V_4(16H_2)$ complexes are found to be 0.07, 0.10 and -0.13 respectively. It indicates that sixteen $H_2$ molecule adsorption on four Sc and four Ti decorated closoborates is energetically favorable at ambient conditions whereas it is unfavorable on four V decorated closoborates. The binding energy of $B_6H_6Sc_4(16H_2)$, $B_6H_6Ti_4(16H_2)$ and $B_6H_6V_4(16H_2)$ complex is found to be 195, 219 and 135 kcal/mol respectively at M06/6-311++G** level indicating that each hydrogen molecule binds to TM atom with energy in a range of 8.4 to 12.2 kcal/mol. It indicates that not only single TM atom decorated $B_6H_6$ complex but four TM atom decorated $B_6H_6$ complexes are also suitable for hydrogen storage though clustering of TM atoms is observed for the latter.

## 4. Conclusions

We have studied hydrogen uptake capacity of transition metal decorated closoborate using M06, B3LYP and MP2 methods and 6-311++G** basis set. The number of hydrogen molecules adsorbed on each complex is the same. Contribution from many-body energies to the binding energy of a complex is studied. Many-body analysis for the three complexes reveals that not only two-body but higher many-body energies are also contributing significantly to the binding energy of respective complex. There are no soft modes for the three complexes indicating that these complexes are quantum mechanically stable. Thermochemistry calculations reveal that adsorption of four $H_2$ molecules on $B_6H_6Ti$ and $B_6H_6V$ is energetically favorable for all the temperatures considered here whereas it is energetically favorable on $B_6H_6Sc$ below 270 K at M06/6-311++G**. Minimum $H_2$ desorption temperature for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$, $B_6H_6V(4H_2)$ is found to be 332 K, 574 K and 472 K respectively whereas maximum desorption temperature for the respective complexes is 650 K, 1288 K and 956 K using M06/6-311++G** level of theory. Averaged adsorption energy is within the proposed range and affected by the functional employed in DFT calculations. In head-to-tail type of dimers of closoborate-TM complexes there is no clustering of TM atom observed and the number of $H_2$ molecules adsorbed per TM atom remains four. $H_2$ molecules adsorbed on sandwiched TM atom are at little longer distance than that on TM atom at one end. In case of four TM atoms decorated closoborate we do observed clustering of TM atoms. Number of $H_2$ molecules adsorbed per TM atom remains the same with two of the sixteen $H_2$ molecules are adsorbed in dissociated form.

## Acknowledgements

Financial support from C.S.I.R., New Delhi, India (Grant 03/1223) is gratefully acknowledged. We thank CDAC, Pune for providing Bioinformatics Resources and Applications Facility (BRAF).

## References

[1] http://www.eere.energy.gov/hydrogenandfuelcells/mypp.

[2] G. Walker (Ed), *Solid state hydrogen storage materials and chemistry*, Woodhead Publ. Ltd., Cambride, England (2008)

[3] D. P. Broom, *Hydrogen Storage Materials The Characterisation of Their Storage Properties*, Springer (2011)

[4] R. A. Varin, T. Czujko and Wronski ZS *Nanomaterials for solid state hydrogen storage*, Springer (2009)

[5] L. J. Ma, J. Jia, H. S. Wu and Y. Ren *Int J Hydrogen Energy* 2013,**38**,16185

[6] M. Li-Juan, J. Jianfeng and H.S Wu *Int J Hydrogen Energy* 2015,**40**, 420

[7] V. Kalamse, N. Wadnerkar, A. Deshmukh and A. Chaudhari *Int J Hydrogen Energy* 2012,**37**,3727

[8] V. Kalamse, N. Wadnerkar, A. Deshmukh and A. Chaudhari *Int J Hydrogen Energy* 2012,**37**,5114

[9] P. Tavhare, V. Kalamse, R. Bhosale and A. Chaudhari *Struct Chem* 2015, **26**, 823

[10] C. S. Liu and Z. Zeng *Phys. Rev. B.* 2009,**79**, 245419

[11] E. Durgun, S. Ciraci, W. Zhou and T. Yildirim *Phys Rev Lett* 2006, **97**, 226102

[12] W. Zhou, T. Yildirim, E. Durgun and S. Ciraci *Phys Rev B* 2007,**76**,085434

[13] N. Wadnerkar, V. Kalamse and A. Chaudhari *Theo Chem Accts* 2010, **127**,285

[14] A. Chakraborty, S. Giri and P. K. Chattaraj *Struct Chem* 2011,**22**,823

[15] A. B. Phillips and B. S. Shivaram *Nanotechnology* 2009,**20**,204020

[16] Y. Okamoto *J. Phys. Chem. C* 2008;**112**,17721

[17] N. He, T. Gao, Z. Zhang, X. Tian and H. Han *J of Mol Struct:THEOCHEM* 2009,**916**,147

[18] V. Kalamse, N. Wadnerkar and A. Chaudhari *J. Phys. Chem. C* 2010, **114**, 4704

[19] N. Wadnerkar, V. Kalamse, A. B. Phillips, B.S. Shivaram and A. Chaudhari *Int. J. Hydrogen Energy* 2011,**36**, 9727

[20] N. Wadnerkar, V. Kalamse and A. Chaudhari *RSC Adv.* 2012, **2**, 8497

[21] Z. Guo, W. Wu and H. Zhang *Struct Chem* 2009, **20**,1107

[22] N. Wadnerkar, V. Kalamse and A. Chaudhari *Int J Hydrogen Energy* 2011,**36**,664

[23] A. I. Martinez *J Nano Research* 2009, **5**,113

[24] P. F. Wecka and T. J. D. Kumar *J Chem Phys* 2007,**126**, 094703

[25] A. B. Phillips, B. S. Shivaram and G. R. Myneni *Int J Hydrogen Energy* 2012,**37**,1546

[26] B. Kiran, A. K. Kandalam and P. Jena *J Chem Phys* 2006,**124**, 224703

[27] Q. Dong, W. Q. Tian, D. L. Chen, C. C. Sun *Int J Hydrogen Energy* 2009,**34**,5444

[28] G. Chen, P. Jena, Y. Kawazoe *J Chem Phys* 2008,**129**,074305

[29] N. Wadnerkar, V. Kalamse and A. Chaudhari *Struct Chem*. 2013,**24**, 369

[30] N. Wadnerkar, V. Kalamse, S. L. Lee and A. Chaudhari *J Comput Chem* 2012,**33**,170

[31] K. Srinivasu and S. K. Ghosh *J Phys Chem C* 2011,**115**,1450

[32] B. Pathak, K. Pradhan, T. Hussain, R. Ahuja, P. Jena *ChemPhysChem* 2012,**13**,300

[33] K. Chang, E. Kim, P. F. Weck and D. Tománek *J. Chem. Phys*. 2011,**134**, 214501

[34] S. A. Shevlina and Z. X. Guo *Appl Phys Lett* 2006,**89**, 153104

[35] M. Li, J. Li, Q. Sun and Y. Jia *J Appl Phys* 2010,**108**, 064326

[36] B. Pathak, K. Pradhan K, T. Hussain, R. Ahuja and P. Jena *ChemPhysChem* 2012, **13**, 300

[37] Q. L. Lu, J. W. Meng, W. J. Song and J. G. Wan *Int J Hydrogen Energy* 2013,**38**,13328

[38] S. Bandaru, N. J. English, A. D. Phillips, J. M. D. MacElroy *J of Comput Chem* 2014, **35**, 891

[39] M. S. Khan and M.S. Khan *Vacuum* 2014,**101**, 151

[40] M. Samolia, T. J. D. Kumar *RSC Adv* 2014, **4**, 30758

[41] J. L. Boone *J Am Chem Soc* 1964,**86**,5036.

[42] C. G. Zhang, R. Zhang, Z. X. Wang, Z. Zhou, S. B. Zhang and Z. Chen *Chem Eur J* 2009, **15**, 5910

[43] R. M. Kumar, J. V. Sundar and V. Subramanian *Int. H. Hydrogen Energy* 2012, **37**, 16070

[44] A. D. Becke *Phys Rev A* 1988,**38**,3098

[45] A. D. Becke *J Chem Phys* 1993,**98**,5648

[46] A. D. Becke *J Chem Phys* 1997,**107**,8554

[47] Y. Zhao and D. G. Truhlar *Theor. Chem. Acc.*, 2008, **120**, 215

[48] C. Møller and M. S. Plesset *Phys. Re*v. 1934, ***46***, 618

[49] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman JR, et al. Gaussian 09. Revision D.01. Wallingford CT: Gaussian Inc.; 2009.

[50] S. S. Xantheas *J Chem Phys* 1994, **100**, 7523

[51] S. S. Xantheas *J Chem Phys* 1995, **102**, 4505

[52] A. Chaudhari, P. K. Sahu and S. L. Lee *J. Chem. Phys.* 2004, **120**, 170

[53] A. Chaudhari and S. L. Lee *J. Chem. Phys*. 2004, **120**, 7464

[54] P. Valiron and I. Mayer *Chem Phys Lett* 1997, **275**, 46

[55] W. Zhou, T. Yildirim, E. Durgun, S. Ciraci S. *Phys. Rev. B* 2007,**76**,085434.

[56] D. R. Lide CRC Handbook of Chemistry and Physics, 75th Ed. New York 1994.

[57] E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold *NBO Program*, ver. 3.1, as implemented in link 607 of GAUSSIAN 09.

**Table 1: Structural parameters (Å) for $TMB_6H_6(4H_2)$ (TM=Sc, Ti, V) obtained at M06/6-311++g** and B3LYP/6-311++g** levels. The values in the parenthesis are obtained using B3LYP method.**

| Assignments | $B_6H_6$ Sc($4H_2$) | $B_6H_6$Ti($4H_2$) | $B_6H_6$V($4H_2$) |
|---|---|---|---|
| $B_6H_6$ -M | 2.29(2.32) | 2.23(2.25) | 2.25(2.28) |
| M-1$H_2$ | 2.21(2.25) | 2.03(2.06) | 1.83(1.83) |
| M-2$H_2$ | 2.26(2.30) | 2.04(2.13) | 1.98(1.99) |
| M-3$H_2$ | 2.24(2.25) | 1.91(1.93) | 1.81(1.84) |
| M-4$H_2$ | 2.14(2.17) | 1.91(1.92) | 1.87(1.94) |

**Table 2: Average hydrogen adsorption energies without ZPE correction (ΔE), with ZPE correction ($\Delta E_{ZPE}$) and Gibbs free energy correction ($\Delta E_G$) at 298.15 K for TM:$B_6H_6$(4$H_2$) (TM=Sc, Ti, V) complex at M06/6-311++g**, B3LYP/6-311++g** and MP2/6-311++g** levels of theory. All energies are in eV.**

| | M06/6-311++g** | | | B3LYP/6-311++g** | | | MP2/6-311++g** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Complex** | **ΔE** | **$\Delta E_{ZPE}$** | **$\Delta E_G$** | **ΔE** | **$\Delta E_{ZPE}$** | **$\Delta E_G$** | **ΔE** | **$\Delta E_{ZPE}$** | **$\Delta E_G$** |
| $B_6H_6$Sc(4$H_2$) | 0.42 | 0.26 | -0.03 | 0.26 | 0.13 | -0.15 | 0.25 | 0.12 | -0.16 |
| $B_6H_6$Ti(4$H_2$) | 0.63 | 0.45 | 0.16 | 0.55 | 0.36 | 0.07 | 0.57 | 0.39 | 0.09 |
| $B_6H_6$V(4$H_2$) | 0.55 | 0.37 | 0.08 | 0.35 | 0.18 | 0.06 | 0.30 | 0.09 | -0.21 |

**Table 3: Calculated minimum ($T_D$Min) and maximum(($T_D$Max) $H_2$ desorption temperatures ( in Kelvin) for $B_6H_6Sc(4H_2)$, $B_6H_6$ Ti($4H_2$) and $B_6H_6V(4H_2)$ complexes.**

| | **M06/6-311++g**** | | **B3LYP/6-311++g**** | | **MP2/6-311++g**** | |
|---|---|---|---|---|---|---|
| **Complex** | **($T_D$Min)** | **($T_D$Max)** | **($T_D$Min)** | **($T_D$Max)** | **($T_D$Min)** | **($T_D$Max)** |
| $B_6H_6Sc(4H_2)$ | 332 | 650 | 166 | 459 | 153 | 357 |
| $B_6H_6Ti(4H_2)$ | 574 | 1288 | 459 | 1186 | 497 | 2295 |
| $B_6H_6V(4H_2)$ | 472 | 956 | 230 | 383 | 115 | ----- |

**Table 4: Selected vibrational modes (in cm$^{-1}$) for TMB$_6$H$_6$(4H$_2$) (TM = Sc, Ti, V) complexes using M06/6-311++g** and B3LYP/6-311++g** levels of theory. The values in the parenthesis are obtained using B3LYP method.**

| **Assignments** | **B$_6$H$_6$Sc(4H$_2$)** | **B$_6$H$_6$Ti(4H$_2$)** | **B$_6$H$_6$V(4H$_2$)** |
|---|---|---|---|
| B$_6$H$_6$-M stretch (sym.) | 403(376) | 410(472) | 336(337) |
| M-H Stretch (sym.) | 544/563/511/685 | 590/693/859/930(934) | 958/999/873(915) |
| M-H Stretch (a sym.) | 1183/1258(859/455) | 1236/1255/1449/1466(779/778) | 1546/1588/1322/1426 |
| H-H Stretch | 3699/3772/3874//3937 | 3274/3314/3448/3644 | 3117/3267/3385/3722 |
| | (4081/3918/4071/3851) | (3137/3293/3426/3500) | (3064/3382/3744/3897) |

**Table 5: Interaction energies and binding energy for $B_6H_6Sc(4H_2)$, $B_6H_6Ti(4H_2)$, $B_6H_6V(4H_2)$ complexes by using the M06/6-311++ G** method.**

| | Interaction Energy (kcal/mol) | | |
|---|---|---|---|
| **Interaction terms** | **$B_6H_6Sc(4H_2)$** | **$B_6H_6Ti(4H_2)$** | **$B_6H_6V(4H_2)$** |
| **Two body** | | | |
| IOM-$H_1$ | -9.98 | -14.63 | -15.20 |
| IOM-$H_2$ | -11.67 | -18.73 | -10.08 |
| IOM-$H_3$ | -9.56 | -21.47 | -14.07 |
| IOM-$H_4$ | -14.16 | -21.59 | -12.92 |
| $H_1$-$H_2$ | 0.25 | 0.58 | 0.93 |
| $H_1$-$H_3$ | -0.11 | -0.05 | 0.42 |
| $H_1$-$H_4$ | -0.11 | -0.07 | 4.28 |
| $H_2$-$H_3$ | 0.31 | 3.34 | 1.21 |
| $H_2$-$H_4$ | 1.43 | 3.41 | -0.12 |
| $H_3$-$H_4$ | -0.12 | 0.16 | 0.58 |
| **Three body** | | | |
| IOM-$H_1$-$H_2$ | 1.18 | 2.37 | -2.85 |
| IOM-$H_1$-$H_3$ | 2.64 | 2.58 | -4.02 |
| IOM-$H_1$-$H_4$ | 0.82 | 2.82 | -3.41 |
| IOM-$H_2$-$H_3$ | 1.13 | 0.13 | -1.22 |
| IOM-$H_2$-$H_4$ | 0.95 | 0.16 | 2.08 |
| IOM-$H_3$-$H_4$ | 1.17 | -0.33 | -3.74 |
| $H_1$-$H_2$-$H_3$ | 0.03 | -0.32 | -0.69 |
| $H_1$-$H_2$-$H_4$ | -0.06 | -0.26 | 0.06 |
| $H_1$-$H_3$-$H_4$ | -0.02 | -0.10 | -0.71 |
| $H_2$-$H_3$-$H_4$ | -0.01 | -0.50 | 0.04 |
| **Four body** | | | |
| IOM-$H_1$-$H_2$-$H_3$ | -2.40 | -1.87 | 0.24 |
| IOM-$H_1$-$H_2$-$H_4$ | -0.95 | -2.05 | -2.52 |
| IOM-$H_1$-$H_3$-$H_4$ | -1.33 | -0.41 | 0.92 |
| IOM-$H_2$-$H_3$-$H_4$ | -1.19 | 1.18 | -2.37 |
| $H_1$-$H_2$-$H_3$-$H_4$ | -0.03 | -0.04 | -0.02 |
| **Five body** | | | |
| IOM-$H_1$-$H_2$-$H_3$-$H_4$ | 1.54 | 1.04 | 2.51 |
| Sum of 2-body | -43.72 | -69.07 | -44.98 |
| Sum of 3-body | 7.83 | 6.56 | -14.45 |
| Sum of 4-body | -5.91 | -3.20 | -3.75 |
| Sum of 5-body | 1.54 | 1.04 | 2.51 |
| **Relaxation energy** | 0.82 | 6.25 | 9.65 |
| Additive energy | -43.72 | -69.07 | -44.98 |
| Non additive energy | 3.46 | 4.39 | -15.69 |
| **Binding energy** | -39.44 | -58.43 | -51.03 |
| **BSSE corrected total energy** | -918.05 | -1006.76 | -1101.28 |

**Caption to Figures**

**Figure 1:** Optimized structures of (a) $B_6HSc(H_2)_4$ (b) $B_6H_6Ti(H_2)_4$ (c) $B_6H_6V(H_2)_4$ at M06/6-311++G** level.

**Figure 2:** Temperature dependent Gibbs free corrected $H_2$ adsorption energy for $B_6H_6Sc(H_2)_4$, $B_6H_6Ti(H_2)_4$ and $B_6H_6V(H_2)_4$ at M06/6-311++G** and B3LYP/6-311++G** levels.

**Figure 3:** HOMO-LUMO gap for $B_6H_6Sc(H_2)_4$, $B_6H_6Ti(H_2)_4$ and $B_6H_6V(H_2)_4$ at M06/6-311++G**, B3LYP/6-311++G** and MP2/6-311++G** levels.

**Figure 4:** Contribution from many-body energies, additive energy, nonadditive energy, relaxation energy to the binding energy of $B_6H_6Sc(4H_2)$ complex. 2B, 3B, 4B, 5B, RE, AE, NE represents total two-body, three-body, four-body, five-body-energy, relaxation energy, additive energy and nonadditive energy respectively.

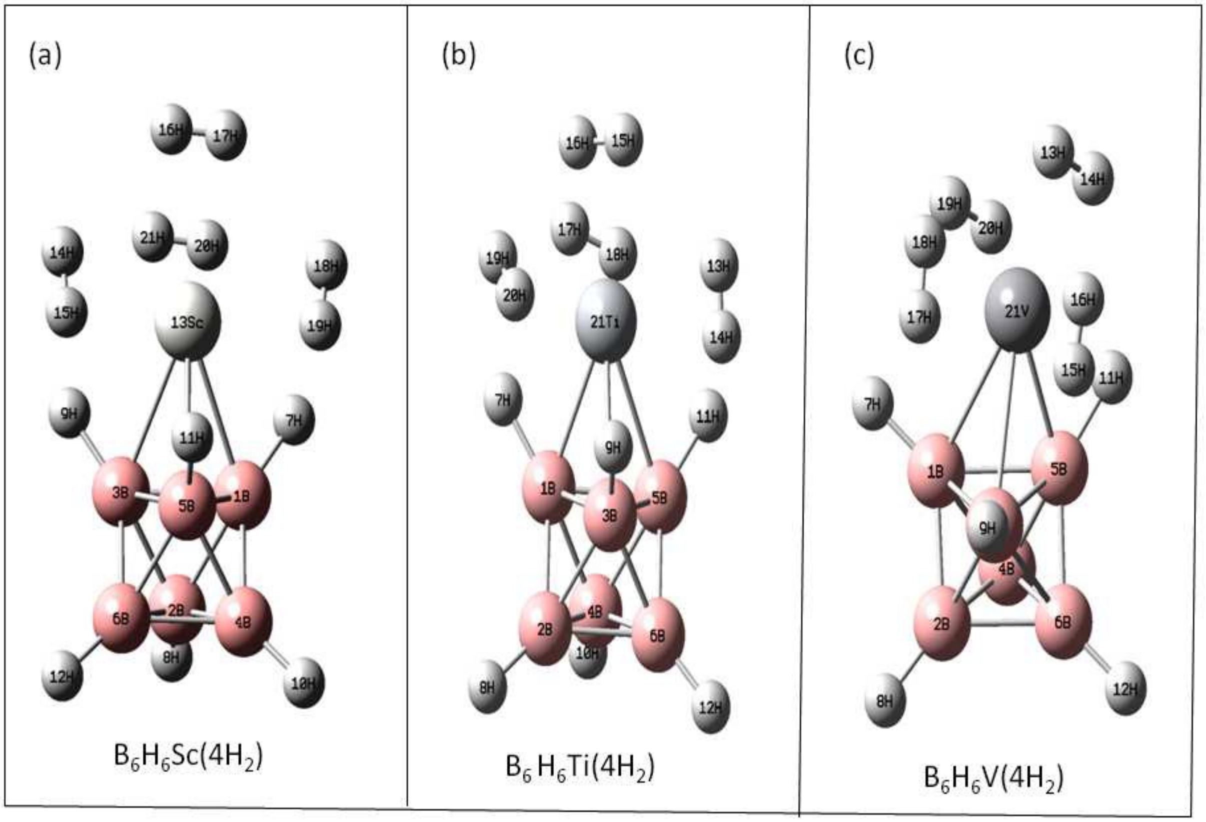
**Figure 5:** Contribution from many-body energies, additive energy, nonadditive energy, relaxation energy to the binding energy of $B_6H_6Ti$ $(4H_2)$ complex. 2B, 3B, 4B, 5B, RE, AE, NE represents total two-body, three-body, four-body, five-body-energy, relaxation energy, additive energy and nonadditive energy respectively.

**Figure 6:** Contribution from many-body energies, additive energy, nonadditive energy, relaxation energy to the binding energy of $B_6H_6V(4H_2)$ complex. 2B, 3B, 4B, 5B, RE, AE, NE represents total two-body, three-body, four-body, five-body-energy, relaxation energy, additive energy and nonadditive energy respectively.

**Figure 7:** Charge on metal atom plotted as a function of number of adsorbed $H_2$ molecules for $B_6H_6Sc(nH_2)$, $B_6H_6Ti(nH_2)$, $B_6H_6V(nH_2)$ (n=1-4) complexes at M06/6-311++G** level.

**Figure 8:** Head-to-tail type dimers of $B_6H_6V$ (a) Before $H_2$ adsorption (b) after $H_2$ adsorption at M06/6-311++G** level.

**Figure 9:** $B_6H_6$ decorated with four Sc atoms (a) before $H_2$ adsorption (b) after $H_2$ adsorption at M06/6-311++G** level.



$B_6H_6Sc(4H_2)$ $B_6H_6Ti(4H_2)$ $B_6H_6V(4H_2)$

**Figure 1**

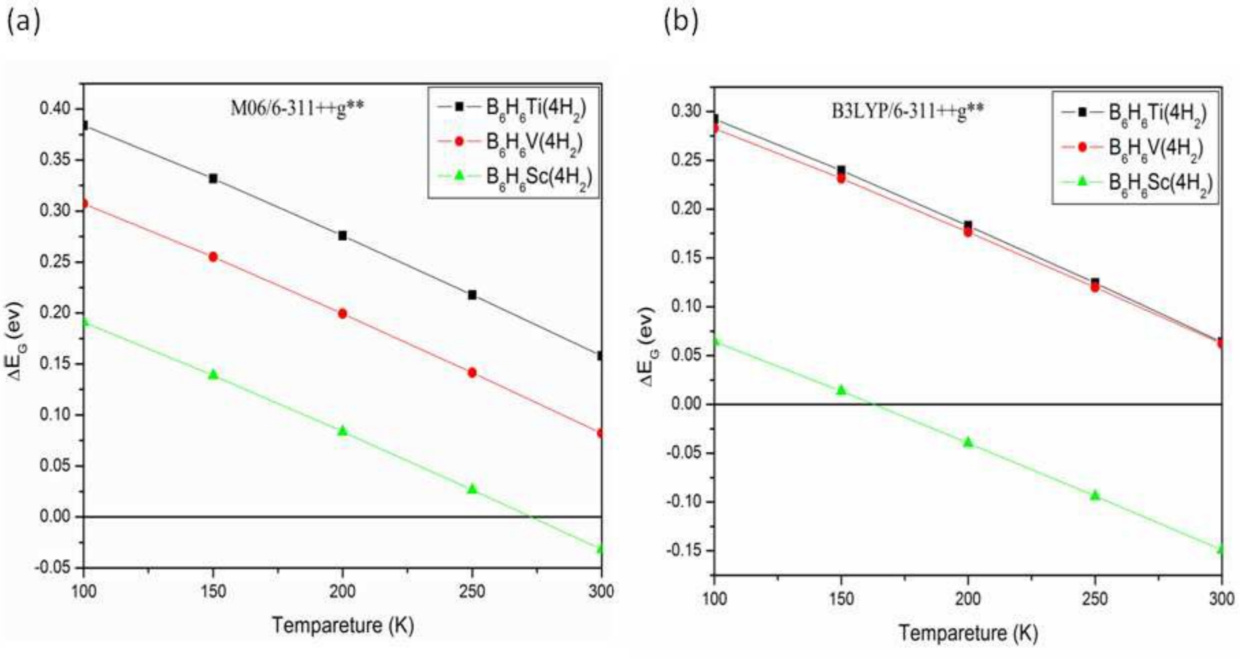

(a)
M06/6-311++g**
B6H6Ti(4H2)
B6H6V(4H2)
B6H6Sc(4H2)
ΔEG (ev)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
100
150
200
250
300
Tempareture (K)
(b)
B3LYP/6-311++g**
B6H6Ti(4H2)
B6H6V(4H2)
B6H6Sc(4H2)
ΔEG (ev)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
100
150
200
250
300
Tempareture (K)

Figure 2

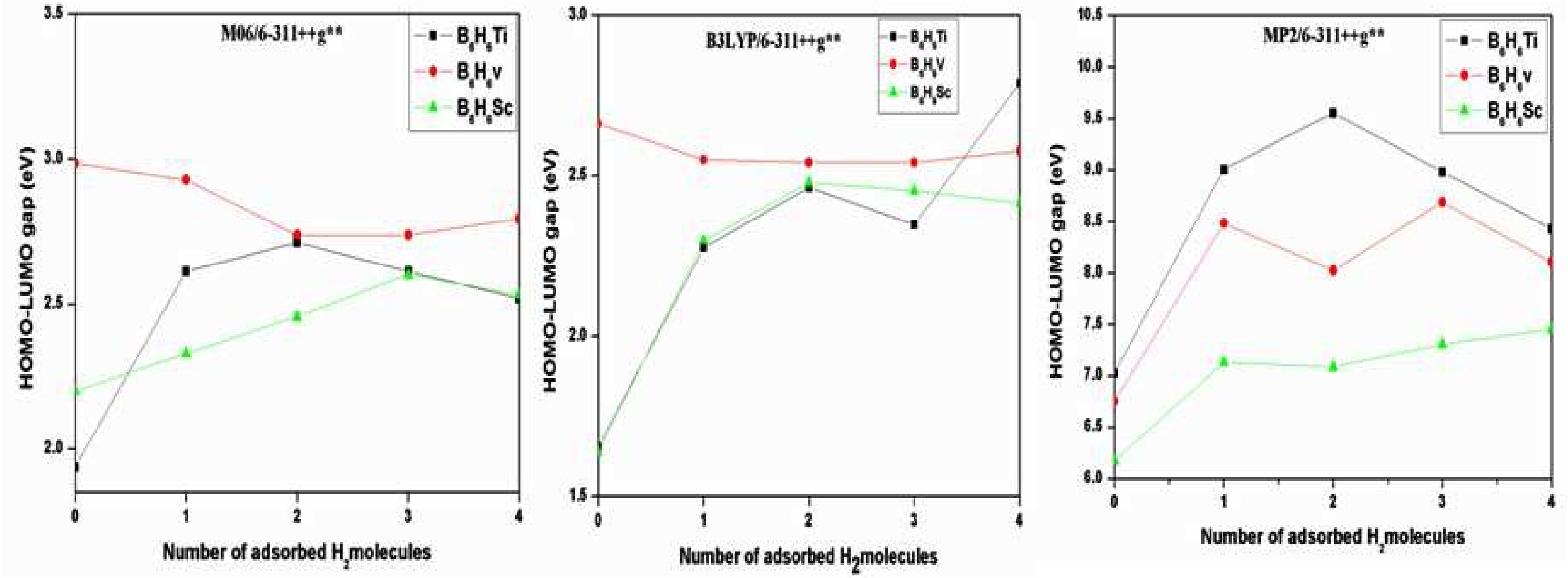

M06/6-311++g**
B3LYP/6-311++g**
MP2/6-311++g**
$B_6H_6Ti$
$B_6H_6V$
$B_6H_6Sc$
HOMO-LUMO gap (eV)
Number of adsorbed $H_2$ molecules
3.5
3.0
2.5
2.0
1.5
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
0
1
2
3
4

**Figure 3**

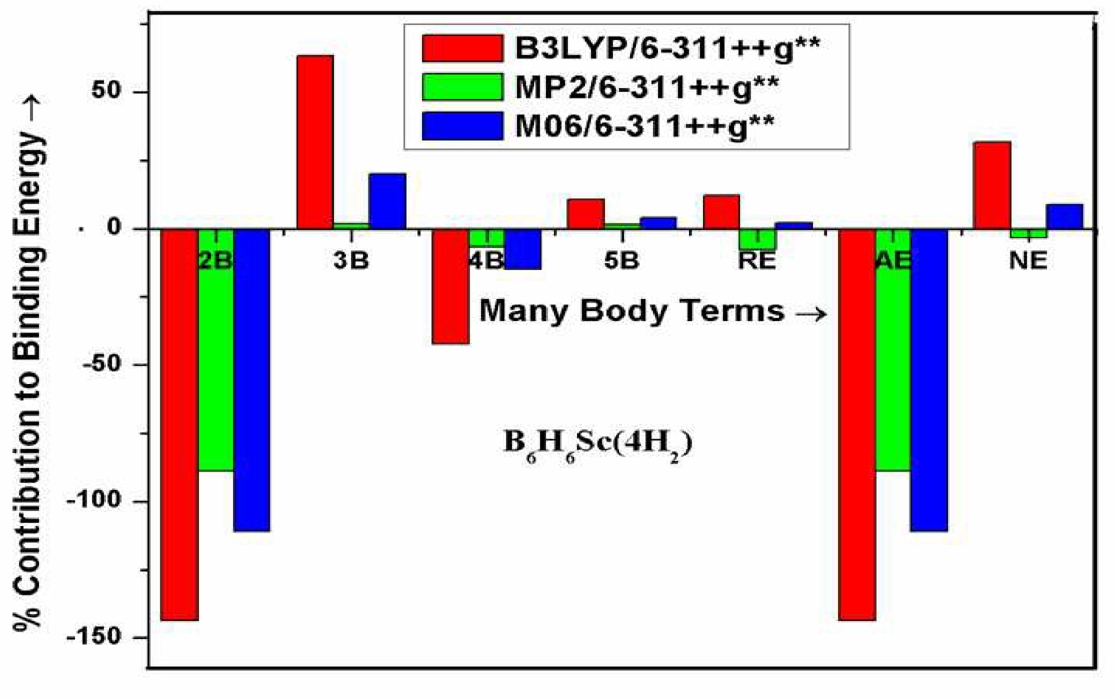

B3LYP/6-311++g**
MP2/6-311++g**
M06/6-311++g**
% Contribution to Binding Energy →
50
0
-50
-100
-150
2B
3B
4B
5B
RE
AE
NE
Many Body Terms →
$B_6H_6Sc(4H_2)$

**Figure 4**

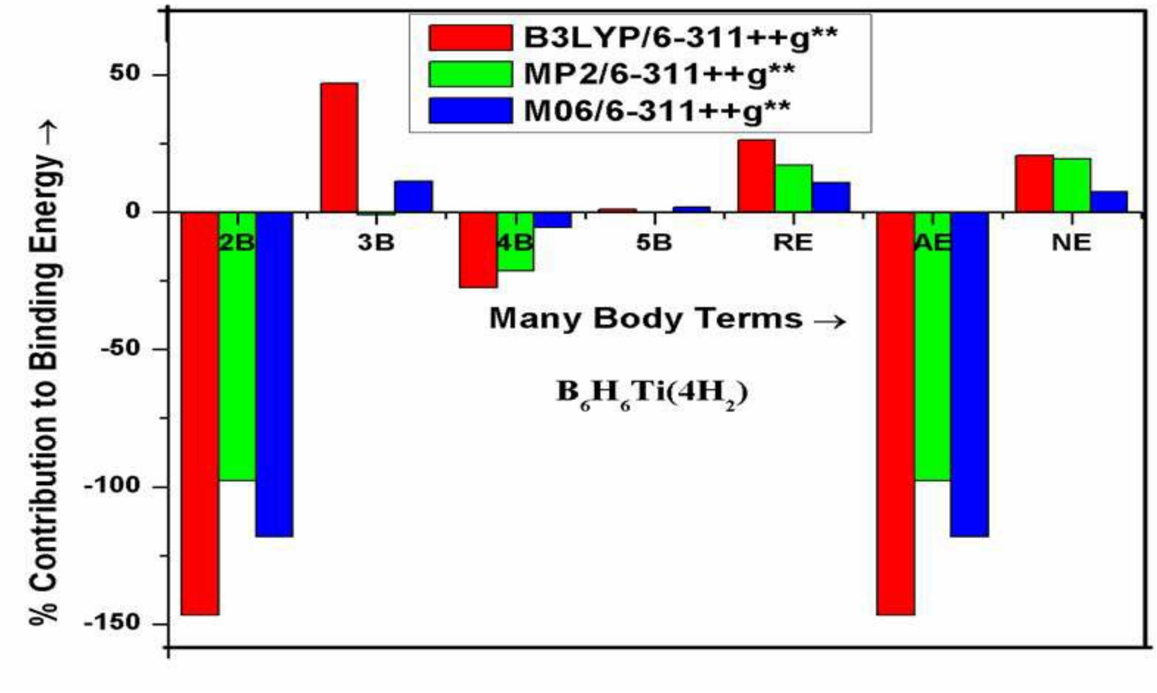
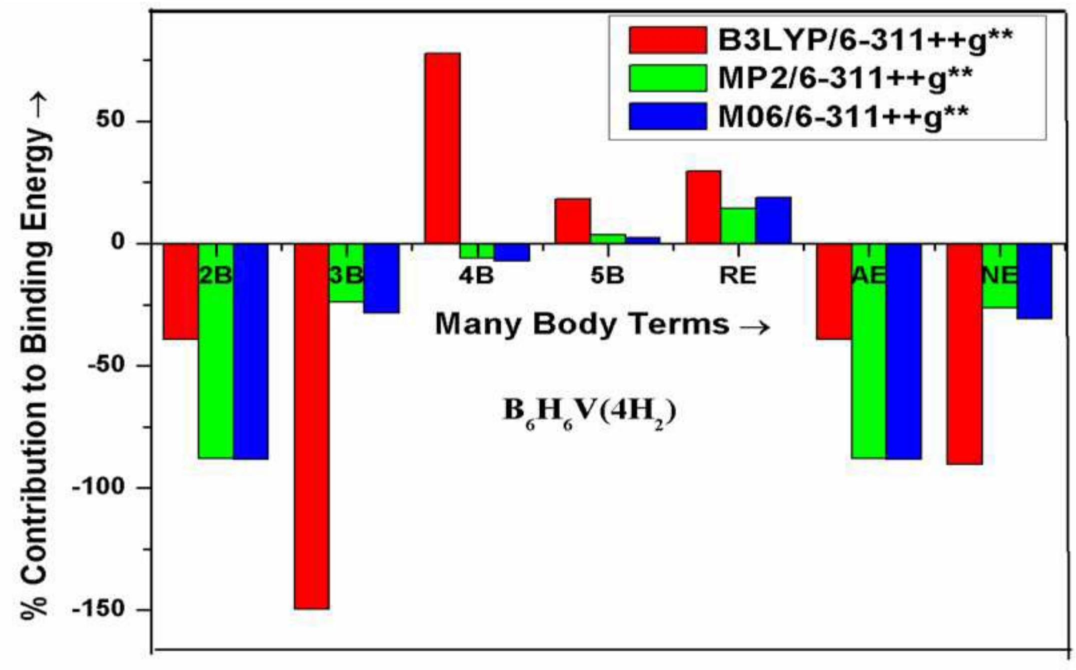

B3LYP/6-311++g**
MP2/6-311++g**
M06/6-311++g**
% Contribution to Binding Energy →
50
0
-50
-100
-150
2B
3B
4B
5B
RE
AE
NE
Many Body Terms →
B6H6Ti(4H2)

Figure 5



B3LYP/6-311++g**
MP2/6-311++g**
M06/6-311++g**
% Contribution to Binding Energy →
50
0
-50
-100
-150
2B
3B
4B
5B
RE
AE
NE
Many Body Terms →
B6H6V(4H2)

Figure 6

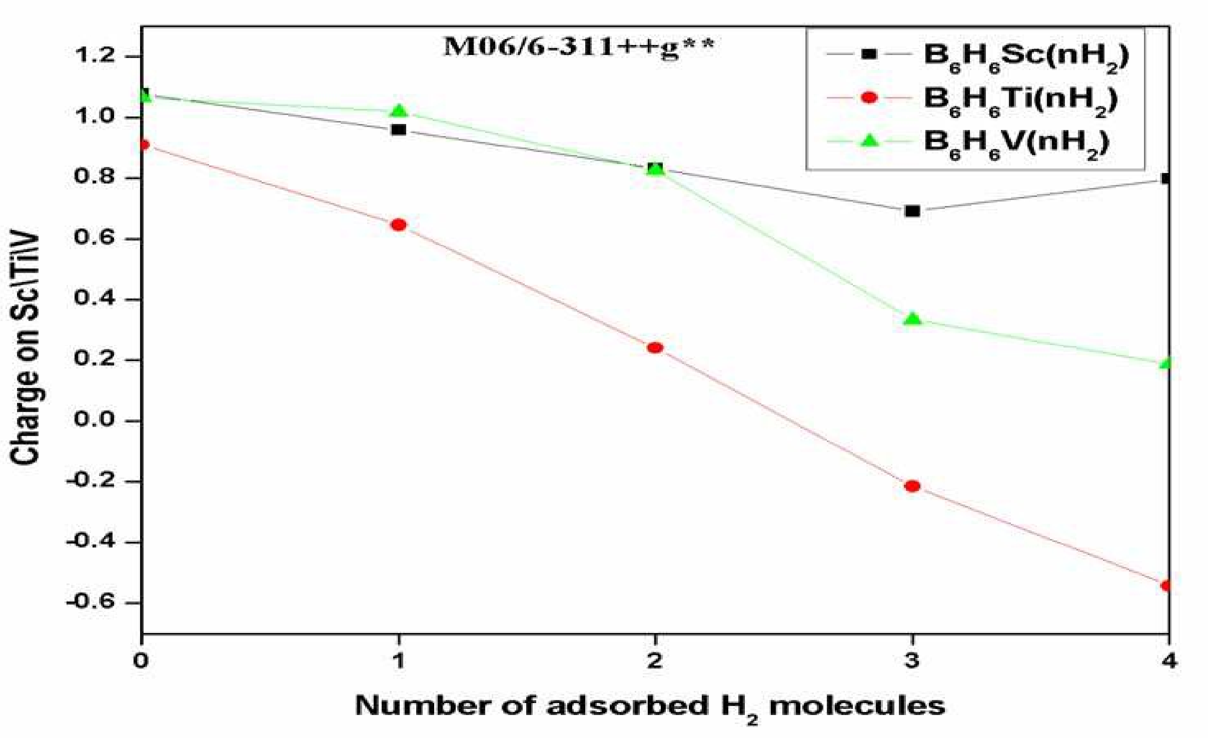

M06/6-311++g**
■ $B_6H_6Sc(nH_2)$
● $B_6H_6Ti(nH_2)$
▲ $B_6H_6V(nH_2)$
Charge on Sc\Ti\V
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
0
1
2
3
4
Number of adsorbed $H_2$ molecules

**Figure 7**

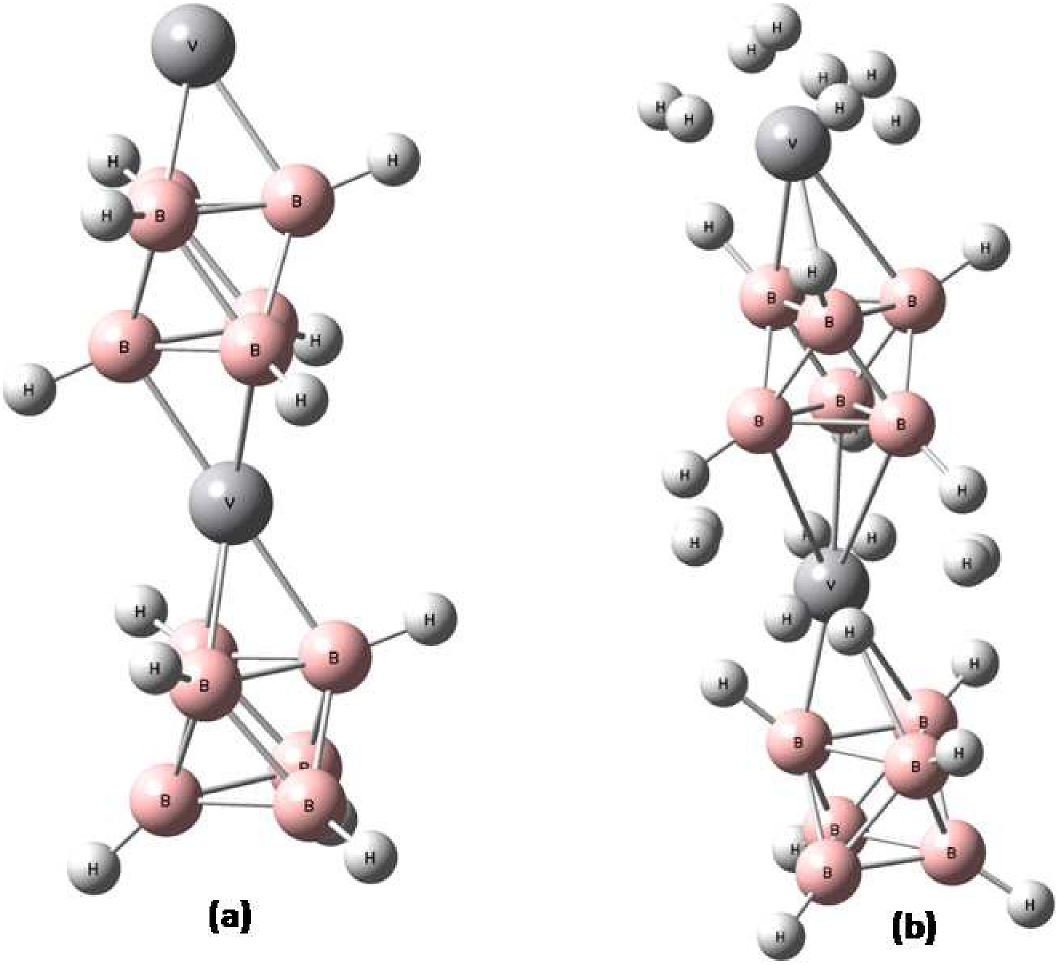


**Figure 8**

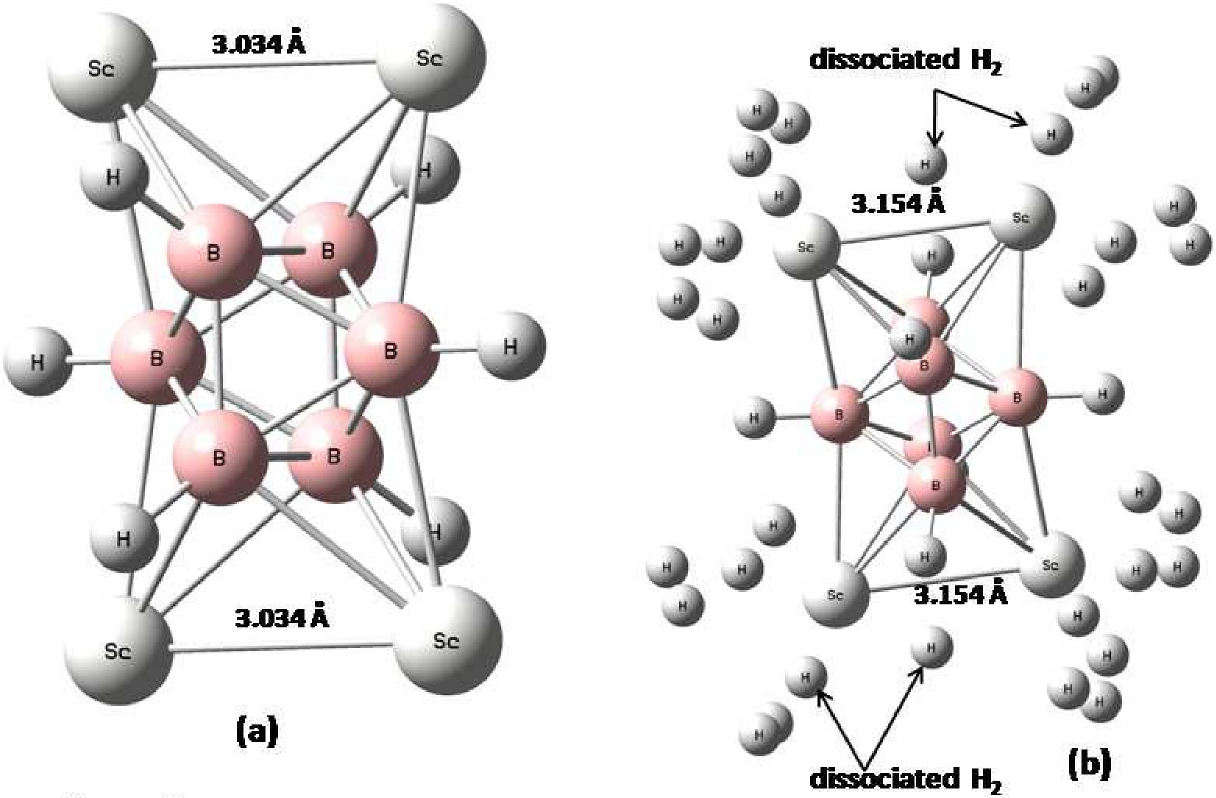

3.034 Å
Sc
Sc
H
H
B
B
H
B
B
H
B
B
H
H
Sc
Sc
3.034 Å
(a)
dissociated H₂
3.154 Å
Sc
Sc
B
B
B
B
Sc
Sc
3.154 Å
H
dissociated H₂
(b)

Figure 9.