Structural properties of metal-benzene, $M_n(benzene)_m$, $M = \text{Ni, V}$ complexes: an ab initio study

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Abstract

Interactions of Ni and V with benzene (Bz)-molecules are investigated using ab initio methods and tight-binding molecular dynamics (TBMD) simulations. The differences in the behavior for Ni and V is found to be consistent with their similar contrasting bonding behavior found in interactions with graphite, $C_{60}$ and carbon nanotubes. 

The interactions of transition metal atoms (TMA) with various low dimension forms of carbon has been the subject of recent experimental and theoretical investigations [1–17]. All these investigations affirm the contrasting bonding behaviors of the 3d-TMA in their interaction with graphite, $C_{60}$, single wall carbon nanotubes (SWCN), and benzene (Bz)-molecules beyond any reasonable doubt. In particular, detailed theoretical studies of the interaction of graphite with TMA have shown that the early 3d-elements (Sc, Ti, V) are energetically more stable at hole sites, while the late 3d-elements (Fe, Co, Ni) are found energetically more stable at atop sites [8,12]. Similarly, the experimental results dealing with the structural properties of small $M_n(C_{60})_m$ clusters, where $M$ denotes a TMA of the 3d-series ($m + n < 10$), have revealed that early 3d-elements form an $M_1[\eta^6-(C_{60})_2]$ bonding configuration, while the late 3d-elements form either an $M_1[\eta^3-(C_{60})_2]$ or an $M_1[\eta^2-(C_{60})_2]$ configuration [1,3,4]. Here $\eta^k$ ($k$ an integer) denotes that there are $k$ ligand atoms (carbon ring atoms) bonded to the metal (M) atoms. Based on these findings, it was proposed that the early 3d-elements form ‘dumbbell’ structures in which the M-atom is sandwiched between six-membered rings of $C_{60}$. It was also proposed that the late 3d-elements form bent or ring-type structures in which the M-atom forms two or three bonds with each $C_{60}$ molecule. These experimental conclusions were theoretically confirmed by recent tight-binding molecular dynamics.
(TBMD) simulations of $M_n(C_{60})_m$, $M = Ni, V$ ($m + n \leq 5$) clusters [9,10].

The experimental results obtained for the interaction of TMA with Bz-molecules have further reaffirmed the contrasting bonding configuration of the 3d-TMAs in their interaction with carbon [5]. Specifically, these results led to the conclusion that the early 3d-elements should form structures in which the M-atom is sandwiched symmetrically between two Bz-molecules in a double $\eta^6$-bonding configuration. On the other hand, it was concluded that the late 3d-elements should form structures of the ‘rice-ball’ type with $\eta^2$- and/or $\eta^1$-bonding configurations. In the latter case, the TMA is encapsulated in an oyster-like opening or within a small volume surrounded by Bz-molecules.

In addition to the contrasting bonding behavior discussed above, the TMAs were found to undergo a significant change in their magnetic moment when they interact with graphite, $C_{60}$, SWCN and Bz-molecules. A striking characteristic feature of this interaction was the quenching of the magnetic moment of Ni on graphite, $C_{60}$, SWCN and Bz-molecules [8,9,13] on the one hand, and the enhancing of the magnetic moment of the early 3d-atoms when supported on Bz-molecules on the other hand [13].

Our recent investigations on the interaction of TMAs with other carbon materials of low dimension have revealed many interesting features [8–11]. This along with the lack of detailed theoretical studies of the organometallic systems in the literature has provided us the necessary motivation to study the $M_n(Bz)_m$ systems in a systematic way in the present work. In this Letter, we report our results of a theoretical investigations of TMA–Bz complexes of the form $M_n(Bz)_m$, $M = Ni, V$ with $m + n \leq 5$, obtained using ab initio computational methods. We also use TBMD relaxations of the systems to complement our ab initio work. The ab initio calculations were performed using the Gaussian 98 program [18]. Structural optimizations were carried out using both ab initio and TBMD methods. While TBMD simulations were used to perform fully symmetry-unconstrained optimizations in all cases, only the smaller clusters were so optimized using ab initio methods due to the computational complexity.

Fig. 1a,b show our ab initio results for the symmetry-constrained ($D_{6h}$) and symmetry-unconstrained optimization of $Ni(Bz)_2$ clusters, respectively. Our calculations show the symmetry-unconstrained relaxed structure to be energetically more stable (by 1.16 eV). It is then apparent from these figures that Ni prefers the $\eta^2$-type bonding with each Bz-molecule following the same general trend found in the bonding configuration of the TMAs with graphite, $C_{60}$ and SWCN. Our results, however, are at odds with the ‘rice-ball’ structure used to interpret the experimental findings [5]. Instead, we find that the two Bz-molecules repel each other and form a Z-like (or step-like) bonding with the Ni atom instead of the ‘oyster-like’ opening of the ‘rice-ball’ structure proposed [5]. It is worth noting that even though we start from a rice-ball like structure, the symmetry-unconstrained relaxation of $Ni(Bz)_2$ results in the structure shown in Fig. 1b, indicating no local energy minimum for the rice-ball structure. As seen in Fig. 1b, the planes of the Bz-molecules are not parallel to each other. Furthermore, the plane containing the C–Ni–C bonds of Ni with one Bz-molecule is rotated by approximately $68^\circ$ with respect to the bonding plane containing the C–Ni–C bonds of the Ni atom with the other Bz-molecule.

We have also performed TBMD optimization of the structure shown in Fig. 1a. This relaxation also resulted in the structure shown in Fig. 1b, showing very good agreement with the ab initio results.

We next repeat our ab initio calculations for the $Ni_2Bz_2$ cluster. Fig. 2a,b, respectively, show the results for the symmetry-constrained ($D_{2h}$) and symmetry-unconstrained optimization of this

Fig. 1. Final structures obtained by performing: (a) symmetry-constrained ($D_{6h}$), and (b) symmetry-unconstrained ($C_1$) relaxations for the $Ni(Bz)_2$ complex using ab initio methods.
The Ni$_3$Bz$_2$ cluster is studied next using the ab initio methods. We performed relaxations both with and without symmetry restrictions. The D$_{6h}$ symmetry-restricted optimized structure is shown in Fig. 3a. Symmetry-unconstrained relaxation starting from the same initial configuration resulted in the structure shown in Fig. 3b. This structure is found to be 1.84 eV more stable than that in Fig. 3a. We have also obtained another stable structure by placing all three Ni atoms between the two Bz-molecules and performing relaxation without any symmetry constraints. The resulting structure shows D$_{3h}$ symmetry and is shown in Fig. 3c. This is the most stable isomer (2.49 eV lower in energy than the structure shown in Fig. 3b) for the Ni$_3$Bz$_2$ cluster among the geometries considered here. These results indicate that the segregation of Ni atoms and the formation of a Ni$_3$ cluster sandwiched between two Bz-molecules are energetically more favorable than the step-like structure of Fig. 3b.

The bonding of Ni atoms to Bz in Fig. 3b is worth a detailed look. The C–C bonds on each Bz-molecule to which Ni atoms bond are not exactly on opposite sides. The alternate single–double bond symmetric configuration of pristine Bz-molecule is broken by the presence of Ni atoms with two Ni atoms saturating two of the C–C double bonds. The configuration in Fig. 3b allows the third C–C double bond to remain without interference from the Ni atoms. This would not be

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**Fig. 2.** Final structures obtained by performing: (a) symmetry-constrained (D$_{2h}$), and (b) symmetry-unconstrained (C$_1$) relaxations for the Ni$_2$(Bz)$_2$ complex. Note that planes of the Bz-molecules are not parallel and can be thought as forming an ‘oyster-like’ opening characteristic of the rice-ball structure.

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**Fig. 3.** Final structures obtained by performing: (a) symmetry-constrained (D$_{6h}$), and (b) symmetry-unconstrained (C$_1$) relaxation for the Ni$_3$(Bz)$_2$ cluster using ab initio methods, (c) symmetry-unconstrained relaxed structure for the Ni$_3$(Bz)$_2$ cluster obtained by placing three Ni atoms between the planes of the Bz-molecules. The relaxed structure has D$_{3h}$ symmetry and is the most stable of the three.
possible had the two Ni atoms bonded on opposite sides of the Bz-molecule. This is supported by our bonding analysis that shows the C–C bond lengths of the Bz-ring to be 1.45 Å except the one double bond with a bond length of 1.38 Å.

The relative stability of the Z-like structure is compared with that of the oyster structure in the case of Ni(2)Bz(3) complex. From our ab initio and the TBMD results (shown in Figs. 4a–c) the oyster structure (Fig. 4a) is found to be isoenergetic with the step-like one (Fig. 4b), the former being more stable by 0.17 eV. The structure obtained by performing a symmetry-constrained optimization (D_{6h}) is shown in Fig. 4c. This structure is found to be less stable than the oyster-like structure by 2.28 eV.

We next study the Ni_{4}Bz_{5} cluster. Due to the large number of atoms, the ab initio symmetry-unconstrained optimization of this cluster is computationally prohibitive. Instead, we perform TBMD relaxation (symmetry-unconstrained) starting from a symmetric configuration. The resulting geometry for this Ni_{4}Bz_{5} cluster is shown in Fig. 5.

A striking feature of this relaxed cluster is the helical step-like (‘cork-screw’) geometry indicating that extended Ni_{m}Bz_{m+1} structures may be stable for large m.

Our ab initio calculations for the Ni_{m}Bz_{n} clusters show that each Ni atom gains approximately 0.80 electrons while the magnetic moment of the Ni atoms is approximately zero (0.04 Bohr magnetons), in agreement with [13].
We repeated the calculations by replacing Ni with V (an early 3d-element). In the case of the V(Bz)_2 cluster, our symmetry-unconstrained relaxation resulted in the same structure as the symmetry-constrained one, i.e., similar to that shown in Fig. 1a in which the V-atom forms \( \eta^3 \)-type bonding configuration with each Bz-molecule. Similar result was obtained in the case of V_2(Bz)_2 complex. That is, symmetry-unconstrained relaxation resulted in a final relaxed structure similar to the symmetry-unconstrained one shown in Fig. 2a.

Our results for Ni_m(Bz)_n and V_m(Bz)_n clusters, thus, reaffirm the contrasting bonding behavior between the early and the late 3d-elements when they interact with Bz-molecules, supporting the conclusion drawn from experiments [5]. Our results, however, do not support the proposed rice-ball structure for all the Ni(m)Bz(n) complexes that we studied. Instead a new structure, namely the Z- or step-like, appears in some complexes to be either more favorable or competing with the oyster structure. In particular, the step-like structure appears more favorable in the case of the NiBz(2) complex; it appears isoenergetic to (and only slightly more stable than) the oyster structure in the case of Ni(2)Bz(3) complex. In the case of Ni(2)Bz(2) and Ni(3)Bz(2) complexes it is found that the structures we find favor the metal segregation and the formation of a metal cluster surrounded (encapsulated) by Bz-molecules. Though the relaxed structure of Ni(2)Bz(2) can be thought of as a distorted oyster type, however, the trend that is more pronounced (as in the case of the Ni(3)Bz(2) complex and in the complexes that form the step-like structure) is that the Ni atoms like to bond at the edges of the Bz-molecules. For larger Ni(m)Bz(n) complexes the step-like structure appears stable. We do not claim, however, that this is the most stable one. The purpose of including this result in the present report is to stimulate future investigations about this structure. Our results, thus, make it clear that the structural outcome appears to be dependent on the size of the Ni(m)Bz(n) complex. It is worth noting that the step-like structure (for \( m < n \)), like the rice-ball one, is consistent.

Additionally, our results also justify the stability of the experimentally traced M_2(Bz)_3 structures which were found very conspicuous in the mass spectra for M = Ni but not for any other 3d-elements.

In our earlier work, we have found qualitative differences in the behavior between Ni and V while interacting with graphite and the C_60 and attributed this to the different occupancies of the metal d-orbitals [10]. The similar contrasting behavior obtained here for Ni and V in their interactions with the Bz-molecule merely reaffirms our earlier reasoning. Other factors such as the variation of the hybridization strength between the metal d-orbitals and the p-orbitals of the Bz-molecules may also contribute to this difference. While the occupancy of the d-orbitals depends on the metal atom and is affected by inter-atomic and intra-atomic charge transfer effects, the hybridization strength can depend on the point group symmetry of the adsorption site (i.e., C_6v for ‘hole’; C_3v for ‘atop’, and C_2v for ‘bridge’ sites), the relaxation near the Bz-molecule, and the metal–Bz-molecule distance [10].

While more simulations involving a greater number of structural configurations for both the clusters examined in the present work and for clusters with other \( n,m \) combinations may be helpful, the present work clearly demonstrates the contrasting behavior of the TMAs with Bz-molecules which is also consistent with the bonding behavior of TMAs with graphite, C_60 and SWCN.

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References