



Probing the stability of the $M_2(\text{Benzene})_3$ $M = \text{Fe, Co, and Ni}$ structures upon electron attachment (deletion) and solvated iron clusters by benzene molecules: $\text{Fe}_2(\text{Benzene})_4$



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ABSTRACT

Rice-ball (RB) and multiple decker sandwich (MDS) structures of clusters containing transition metal atoms and benzene (Bz) molecules, $[M_2Bz_3]^{\pm 1}$ $M = \text{Fe, Co, and Ni}$ were studied by means of density functional theory all-electron calculations including dispersion correction as in the BPW91-D2 method. A RB geometry was identified for the ground state (GS) of neutral Fe_2Bz_3 . However, consistent with reported experimental results, RB and MDS structures may occur for the Fe_2Bz_3^- ion. The RB and MDS isomers of Co_2Bz_3 are degenerate; they have comparable ionization energies; this finding is in agreement with the experimental results, where two isomers were identified also. Experiment and theory suggest that the Co_2Bz_3^- ion has similar geometry, MDS, as the neutral parent. RB and MDS motifs are degenerate for both Ni_2Bz_3 and Ni_2Bz_3^+ . A RB form is predicted for Ni_2Bz_3^- . In the GS of Fe_2Bz_4 one benzene molecule was found in the outer region of the RB Fe_2Bz_3 subcluster; it presents a binding energy (D_0) of 4.6 kcal/mol, being originated from weak van der Waals forces. Thus, bridging the internal ligands, the fourth molecule has solvent behavior in the singlet Fe_2Bz_4 GS. Likewise, 3 + 1 MDS isomers of Fe_2Bz_4 were found at higher energies, ≈ 13.1 kcal/mol, from the GS. In Fe_2Bz_4^- , the RB motif yields the GS with a D_0 of 6.7 kcal/mol for the solvent unit. Having a D_0 of 9.0 kcal/mol for such moiety the MDS Fe_2Bz_4^- ion is near in energy (3.6 kcal/mol) to the Fe_2Bz_4^- GS. The GS has an electron affinity (EA) of 0.40 eV. Notably, the MDS isomer has a larger EA (0.83 eV). The outer molecule in the 3 + 1 RB GS is stabilized by a network of dipole $\text{C}^{\delta-}-\text{H}^{\delta+}-\text{C}^{\delta-}$ interactions, formed between the external (internal) hydrogen atoms and the π -electrons of the internal (external) benzene rings. Dipole $\text{C}-\text{H}_{\text{int}}^{\delta+}-\text{C}_{\text{ext}}^{\delta-}$ interactions predominate in the 3 + 1 MDS isomers.

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1. Introduction

The interaction of transition metal (TM) ions with organic molecules is an important issue of research in chemistry and biology [1]. For example, the functionality of biological molecules depends strongly on their three-dimensional structures, which are mainly determined through noncovalent interactions with TM ions (i. e. cation- π , anion- π , as well as π - π) and solvation (how the O-H, N-H, and C-H groups of the ligands interacts with the metal and with other molecules around the TM ion). Recently developed experimental methods permit the synthesis and characterization,

in the gas phase, of mixed clusters containing transition metal (TM) atoms and different kind of molecules [1–9]. This is very important, because allows the study of the fundamental metal–ligand interactions, in the absence of solvent effects, responsible for the structural and electronic properties of such compounds. For clusters formed between TMs and benzene (Bz) molecules, Kaya et al. found that earlier TMs prefer multiple decker sandwich (MDS) structure, showing alternating layers of ligands and metals [2]. Later TMs tends to produce rice-ball (RB) geometries with the TM cluster fully covered by Bz units [1]. Other fact is the rich structure contained in the mass spectra of Fe_nBz_m and Co_nBz_m , increasing exceptionally for Ni_nBz_m ; whereas less structure was found for Sc–Mn, see Fig. 1 of reference 2. However, the study of negatively charged TM clusters with benzene molecules is scarce. The mass spectra for the Fe_nBz_m^- anions record several bands around the

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Fe_2Bz_m^- compositions [10]. Note the strong peak of Fe_2Bz_3^- , Fig. 1 of Reference 10, signifying an enhanced stability for this ion. The question is if such plethora of spectral bands could be accounted in terms of RB and MDS motifs or if there are other structures of the clusters. Characterization of Fe_2Bz_3^- was done by anion photoelectron spectroscopy; in this way were determined electron affinities (EA) and photoelectron spectra of these complexes [10]. Lately, Duncan et al. have found that $\text{Ni}^+(\text{Bz})_{3 \leq m}$ clusters have outer benzene moieties that are weakly bond, acting essentially as solvent species as they are not directly bonded to Ni^+ [11,12]. Competition between RB and MDS states was studied by experiment and theory for TM_2Bz_3 , where the TM atoms or dimers are covered by Bz rings [13–15]. Specifically, a RB low-lying state was determined for Fe_2Bz_3 , whereas the MDS motif was located near in total energy, at 6.6 kcal/mol [15]. An interesting point is on the possibility for the addition of an extra benzene molecule to Fe_2Bz_3 , emerging the question on the location of such molecule in Fe_2Bz_4 . That is, if it is directly attached to the iron atoms, in MDS, or to Fe_2 , in RB, or if it is placed in the external region, far away from the iron sites. Which of these structures has more ability for the absorption of benzene is important, since it is related with the competition of the metal–metal and metal–ligand bonding arising in Fe_2Bz_4 .

The goal of this work is to study, using density functional theory (DFT), the low-lying states of Fe_2Bz_3 , Co_2Bz_3 and Ni_2Bz_3 and the absorption of one benzene molecule on the structures of Fe_2Bz_3 . The nature of the Fe_2Bz_3 –Bz interaction responsible for the absorption event will be depicted. It will be analysed if the Fe–C bonding, in the RB isomer, allows the preservation of the Fe_2 molecule. Indeed, an interesting point concerns with the experienced changes of the structural and electronic properties of the magnetic Fe_2 dimer, being produced by the attachment of four benzene molecules. Attachment of benzene molecules on the alternating layers of ligands and metals of the MDS motif is also an important channel of growth. As will be shown, the potential energy surface (PES) of Fe_2Bz_3 is intricate, arising many possibilities for the absorption. It was found that the RB structures are the ones of lowest energy for neutral Fe_2Bz_4 . For Fe_2Bz_4^- ions the RB motifs define also the ground state (GS). But in this case the MDS structures are near in total energy to the GS, in such way that both RB and MDS isomers may contribute to the observed properties of the negatively Fe_2Bz_4^- charged complexes. Energetic properties like ionization energies and electron affinities will be addressed also.

2. Computational procedure

Lowest energy structures of neutral and charged $[\text{M}_2\text{Bz}_3]^{\pm 1}$ $\text{M} = \text{Fe}, \text{Co},$ and Ni and Fe_2Bz_4 clusters were studied through all-electron calculations realized with the BPW91 method [16,17]. Orbital 6–311++G(2d,2p) basis sets were used for the H(6s2p)/[4s2p], C(12s6p2d)/[5s4p2d], Fe (15s11p6d2f)/[10s7p4d2f], Co(15s11p6d2f)/[10s7p4d2f] and Ni(15s11p6d2f)/[10s7p4d2f] atoms [18–21]. The quantum chemistry software Gaussian-09 was used [22]. Long-range electron correlation accounting for van der Waals forces was included through the semiempirical dispersion-corrected DFT-D2 approach [23,24]. This method is referred as BPW91-D2. RB and MDS candidates of different multiplicities ($M = 2S + 1$, S is the total spin), were inspected for the M_2Bz_3 , $\text{M} = \text{Fe}, \text{Co},$ and Ni species. Several absorption modes were explored for the addition of an extra benzene molecule to the RB and MDS isomers of the Fe_2Bz_3 subcluster. 1) Not directly attached to the metal, the molecule was approached perpendicularly to one benzene ring of Fe_2Bz_3 . 2) The external ring approaches in a parallel way to an internal ligand. These modes, involving the interaction of two benzene rings, resemble the tilted T-shape and PD states of the benzene dimer. 3) The extra molecule

is attached either on two or three benzene ligands of the RB Fe_2Bz_3 geometry. 4) It was placed in parallel way to the alternate layer of metal and ligands of the MDS Fe_2Bz_3 motif. The structural and electronic relaxation procedure was performed without imposing symmetry constraints. The located optimised states were confirmed to be true local minima on the PES by estimating the normal vibrations within the harmonic approximation with the following computational protocol. Using an ultra-fine grid, tight convergence was required for the total energy, minimized to 10^{-8} a.u.; while the geometries were optimized with a 10^{-5} a. u. threshold for the RMS forces. Tight tolerances are needed, because neutral and charged M_2Bz_3 and Fe_2Bz_4 species have several isomers of different geometry and multiplicity within a thin energy range, complicating the location of the low-lying states. The structures reported in Figs. 1–9 are for the true minima since they have positive frequencies. A natural bond order (NBO) population analysis was performed for the optimized structures [25]; gross atomic charge distributions with this approach were found for a qualitative explanation of the charge transfer effects. It should be mentioned that BPW91 describes accurately the metal–metal interaction in Fe_n clusters [26,27], which is important for the study of iron particles interacting with benzene molecules [28,29]. Distortions of the benzene rings in M_2Bz_3 and Fe_2Bz_4 will be referred to the C–C and C–H distances, 1.398 and 1.089 Å, estimated for bare benzene at this level of theory. Including zero-point vibrational energy (ZPVE) for the total energies (E_t) of the GS of Fe_2Bz_3 , Fe_2Bz_4 , and Bz, the binding energy (D_o) for the extra added molecule was determined through the equation: $E_t(\text{Fe}_2\text{Bz}_3) + E_t(\text{Bz}) - E_t(\text{Fe}_2\text{Bz}_4)$.

3. Results and discussion

3.1. Low lying states of Fe_2Bz_3 , Fe_2Bz_3^- and Fe_2Bz_3^+

A RB structure in a singlet state, shown in Fig. 1a, was found for the GS of neutral Fe_2Bz_3 ; where Fe_2 presents a lengthened bond length, of 2.762 Å; without dispersion, BPW91 yields 2.817 Å. The BP86 method gives also singlet RB geometry, with a Fe–Fe distance of 2.818 Å, for the GS of Fe_2Bz_3 [15]. Structures of higher spin (triplet, quintet, and septet) were found at higher energies. For instance, the RB triplet was located at 15.5 kcal/mol (BPW91-D2) or at 13.3 kcal/mol (BPW91). Which is in agreement with the obtained results using BP86: a triplet is situated at 16.0 kcal/mol [15].

The BPW91-D2 method indicates a septet, with a bond length of 2.008 Å, for the GS of Fe_2 . Hence, absorption of three benzene molecules strongly perturbs the structural and electron properties of Fe_2 . In Fe_2Bz_3 the **A** and **B** ligands show η^6 –coordination with the Fe_a and Fe_b atoms, respectively, which are originated from the overlap of the 3d electrons and the π -clouds of the benzene molecules. The symmetrical η^6 coordination yields small deviations from planarity for the **A** and **B** rings. The **C** molecule, forming three Fe–C bonds with each Fe atom, has clear deviations from planarity. Indeed, **C** has chair shape in the GS of Fe_2Bz_3 . The metal–ligand, η^6 – η^3 , and metal–metal bonding indicates that each iron atom fulfill the 18 electrons rule, accounting for the observed stability of Fe_2Bz_3 : as seen in Fig. 2 of Reference 2 the mass spectra for Fe_nBz_m shows a strong peak at the (2, 3) composition. Moreover, through the Fe–C bonding is done the transference of 0.78 electrons (**e**) towards the metal. The resulting $\text{Fe}_2^- \text{Bz}_3^+$ configuration add to the stability of the complex.

Electron addition produces a stabilization of 7.2 kcal/mol (0.31 eV) for the lowest energy RB state, a doublet, of Fe_2Bz_3^- . As seen in Fig. 1b, the extra electron produces significant structural relaxation, because larger metal–metal separation, of 3.108 Å, was found in the Fe_2Bz_3^- ion. Even more, the distance between the Fe_a (Fe_b) site and the center of the **A** (**B**) ring is shorter in the anion, as

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