

## Structures and Infrared Spectroscopy of Metal Cation-Borazine Complexes

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### Abstract

Borazine ( $B_3N_3H_6$ ) is known as 'inorganic benzene' because of a planar  $B_3N_3$  ring with equivalent B-N distance. The lone pair from N in the ring delocalize to the adjacent p-orbital of B which leads to a conjugated system. Even though metal-benzene complexes have been studied extensively as models for cation- $\pi$  interactions and organometallic bonding, similar systems with borazine is relatively scarce. Here, we present a density functional study on metal cation-borazine complexes focusing on geometric and electronic structures and their effects on infrared spectra. We have chosen Al, V, Mn, and Zn cations with various d-configurations which provide models for study donor-acceptor complexes. Among these four metal complexes,  $Al^+$  and  $Mn^+$  prefer to bind to  $\pi$ -cloud on top of the borazine ring. On the other hand,  $V^+$  and  $Zn^+$  bind to B and N, respectively. Infrared spectra of these complexes show four major bands: N-H-, B-H stretches and B-N-B ring and scissoring modes. Interactions of Al and Mn barely shift these band positions in the respective complexes as compared to those in isolated borazine, because of less cation- $\pi$  interactions. On the other hand,  $V^+$  and  $Zn^+$  significantly perturb the borazine ring resulting shifts in infrared bands in these systems.

**Keywords:** density functional theory, infrared spectroscopy, metal-ligand complexes

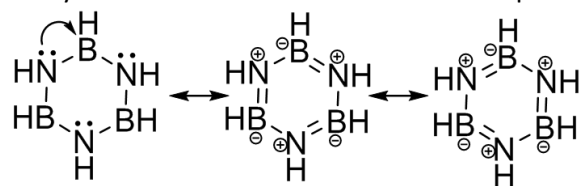
### Introduction

Understanding the structure and bonding of metal-benzene complexes is the key to answer some fundamental questions in organometallic chemistry.<sup>1</sup> These systems have been synthesized by laser vaporization techniques and studied via infrared spectroscopy.<sup>2-11</sup> Quantum chemical calculations have also been extensively employed to these species which provided geometric and electronic structural information.<sup>12-15</sup> On the other hand, similar complexes of metals with borazine have been relatively unexplored. Borazine ( $B_3N_3H_6$ ), also known as 'inorganic benzene', is isoelectronic with benzene and consists of a planar  $B_3N_3$  ring with equivalent B-N distance (see Figure 1). The resonance structure of borazine is sketched in Scheme 1 which shows that the lone pair from N can delocalize to the adjacent empty p-orbital on B, making a conjugated system. The aromaticity of borazine is less than that of benzene as computed by aromatic stabilization energy (ASE). While ASE of benzene is found to be 92.5-150.6  $\text{kJmol}^{-1}$ , the

same value for borazine is 41.8-46.4  $\text{kJmol}^{-1}$ .<sup>16</sup> Even though aromaticity of borazine is less than that of benzene, presence of an electron rich N and a deficient B atom in the ring can potentially form donor-acceptor complexes with suitable species.<sup>16</sup> Transition metals with various d-electron configurations are ideal candidates for these complexes, and can provide useful structure-bonding information.

Main group metal (Li and Ca)-borazine complexes have been studied by Kang using density functional theory, where he compared the metal complexes of benzene and borazine.<sup>17</sup> The study focused on the effect of differences in aromaticity of benzene and borazine on these systems. In addition, the author has also discussed the role of empty d-orbitals. Guo and coworker have studied 3d transition metal doped borazine systems focusing on hydrogen storage properties, and found that titanium is the optimum dopant.<sup>18</sup> In the present work, we present a density functional

study of metal cation-borazine complexes.



**Scheme 1.** Resonance structures of borazine.

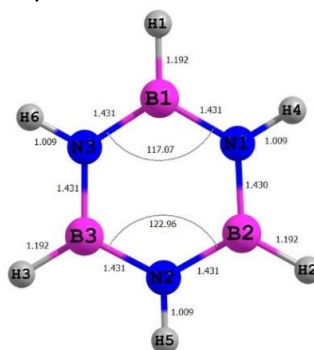
### Computational Methodology

$M^+$ -borazine ( $M^+ = \text{Al}, \text{V}, \text{Mn}, \text{Zn}$ ) complexes were studied using density functional theory (DFT).<sup>19</sup> The structures and vibrational frequencies were computed using Becke, Lee-Yang-Parr (B3LYP)<sup>20</sup> exchange correlation functional and 6-311+G (d, p) basis set. Vibrational frequencies are scaled by a factor of 0.9613 as recommended for this functional and basis set.<sup>21</sup> Bands in computational spectra are given 10  $\text{cm}^{-1}$  fwhm Lorentzian line shape. Due to the open d-shell structure, transition metal systems have many spin-multiplet structures within a narrow energy range. Although the density functional theory can yield the lowest-energy state in each particular symmetry (spatial and spin) channel, the calculations will tend to favor systems with highest spin multiplicities. Therefore, higher level theories electronic wave functions are treated as multistate determinates would be necessary to

validate the accuracy of DFT. However, such methods (e.g., MCSCF, CASSCF, etc.) are computationally intensive. Bauschlicher and Maitre used the infinite order coupled cluster method with all singles and doubles and noniterative inclusion of triple excitations (CCSD(T)) for transition metal-oxide complexes.<sup>22</sup> The density functional results agree very well with CCSD(T) results as pointed out by Blanco and coworkers.<sup>23</sup> Metal-borazine complexes have not been studied as extensively as metal-benzenes. Therefore, here, we used a computationally cheaper method which would give us relatively reliable results.

### Results and Discussion

Figure 1 depicts the structure of borazine showing B-N, B-H, N-H bond lengths, and N-B-N, B-N-B bond angles. Borazine has a planar structure with equivalent B-N bond length (1.431 Å). B-H and N-H bond lengths are computed to be 1.192 and 1.009 Å, respectively. Because of the lone pair on nitrogen, the B-N-B angle is 5° wider than the N-B-N angle. There are various metal binding sites on borazine, e.g., cation can attach either on top of the  $\pi$ -cloud, on top of either B or N, on B-H or N-H making metal-H sigma bonds. For each metal, initial geometries were started from these locations and optimized without any constraints.



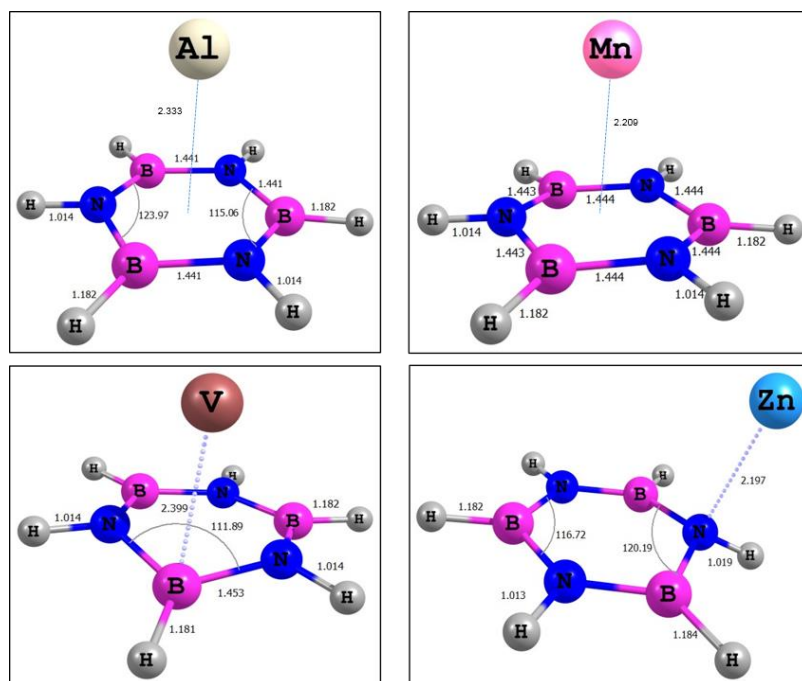
**Figure 1.** Computed structure of borazine with bond lengths and angles. Bond lengths are in angstroms, angles are in degrees.

Figure 2 shows the structures of various metal cation-borazine complexes. For each metal, optimized geometries show only one stable

structure even though different initial geometries were considered.  $\text{Al}^+$  and  $\text{Mn}^+$ -borazine complexes show cation- $\pi$  structures where

cations attach on top of the  $\pi$ -cloud. The lengths between the borazine  $\pi$ -cloud with Al and Mn are computed to be 2.333 and 2.209 Å.  $V^+$  and  $Zn^+$  prefer to bind on top of B and N, respectively. In the cases of  $Al^+$  and  $Mn^+$ -borazine complexes, the B<sub>3</sub>N<sub>3</sub> planar structure remains almost intact. The B-N bond distance slightly reduced from 1.441 in

isolated borazine to 1.431 Å in the respective complexes. The N-H and B-H bond lengths are also slightly different than those of isolated borazine (NH/BH bond lengths in these complexes are  $\sim$ 1.009/1.182 Å as compared to  $\sim$ 1.014/1.192 Å in borazine). The B<sub>3</sub>N<sub>3</sub> structures are slightly puckered in  $V^+$  and



**Figure 2.** Structures of  $M^+$ -Borazine complexes showing bond lengths and angles. Bond lengths are in angstroms, angles are in degrees.

$Zn^+$ -borazine complexes due to interactions of metal ions with B and N, respectively. For  $V^+$ -Bz, B attached to  $V^+$  is  $15^\circ$  out of the plane; and this deviation for N in  $Zn^+$ -Bz is  $8^\circ$ . The N-B-N angle is reduced to  $111^\circ$  in  $V^+$ -Bz from that of isolated borazine ( $117^\circ$ ). The B-N-B bond angle in  $Zn^+$ -Bz is also slightly smaller ( $120^\circ$ ) than that of isolated borazine ( $123^\circ$ ).

In order to discuss the structural parameters in terms of electron distributions within a complex, the molecular orbitals (HOMOs and LUMOs) of  $Al^+$ -,  $V^+$ -, and  $Zn^+$ -borazine complexes are shown in Figure 3. The  $d$ -orbital electronic configuration in transition metals significantly influence the binding preferences. The electronic configuration

of isolated  $Al^+$  is  $[Ne]3s^2$  with  $^1S_0$  state. The HOMO of  $Al^+$ -borazine (left inset in the upper trace of Figure 3) shows the interaction between the Al cation with the  $\pi$ -cloud. On the other hand, LUMO shows the delocalization of the  $s$ -electron in to the empty B-based  $p$ -orbitals. The isolated V cation has a configuration of  $[Ar]3d^4$  with a  $^5D_0$  state. As shown, the HOMO and LUMO of  $V^+$ -borazine (middle trace) show interactions between metal based  $d$ -orbital to B-based  $p$ -orbitals. Since  $Mn^+$  has a half-filled  $[Ar]3d^5$  configuration, the  $d\pi$ - $p\pi$  interactions significantly reduced and MOs (not shown in Figure) resemble to those of  $Al^+$ -borazine.  $Zn^+$  has a closed shell  $[Ar]3d^{10}$  configuration, but instead of a cation- $\pi$

interaction, it prefers to bind to N because of  $d\pi-p\pi$  interactions. favorable

	Energy	Binding Energy
Borazine	-242.7485114	0
Al <sup>+</sup> -Borazine	-484.9479223	21.3
V <sup>+</sup> -Borazine	-1186.4634797	39.5
Mn <sup>+</sup> -orazine	-1393.479271	24.8
Zn <sup>+</sup> -Borazine	-2021.8088744	33.5

**Table 1.** Energies (in Hartrees) and binding energies (kcal/mol) of M<sup>+</sup>-Borazine complexes.

	N-H stretch	B-H stretch	Ring modes	Scissor
Borazine	3490	2512	1340/1424	898
Al <sup>+</sup> -Borazine	3440	2594	1404/1312	923
V <sup>+</sup> -Borazine	3454/3433	2596	1403/1362/1285	929
Mn <sup>+</sup> -Borazine	3435	2599	1400/1301	923
Zn <sup>+</sup> -Borazine	3453/3369	2579	1447/1373/1321	942

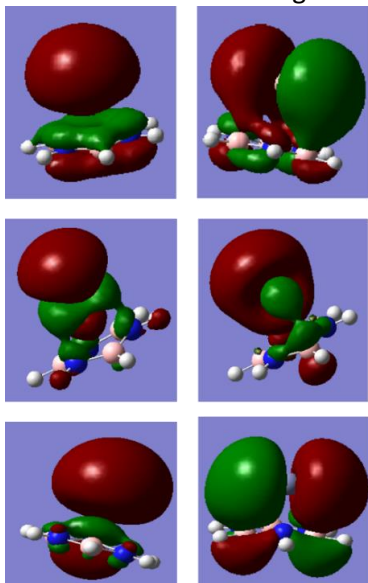
**Table 2.** Vibrational frequencies of borazine and M<sup>+</sup>-Borazine complexes computed at B3LYP/6-311+G (d, p) level. Harmonic frequencies are in cm<sup>-1</sup> and scaled by a factor of 0.9613.

The binding energies of M<sup>+</sup>-borazine complexes are shown in Table 1. As explained in the above paragraph, both Al and Mn has only electrostatic interactions and therefore binding energies are much less than the other transition metals. V<sup>+</sup>-borazine apparently has the highest binding energy due to more favorable interaction followed by Zn<sup>+</sup>-borazine.

Figure 4 depicts vibrational spectra of the isolated gas phase borazine, along with those of M<sup>+</sup>-borazine complexes. The infrared spectrum of borazine consists of four main bands. B-H and N-H stretches are computed at 2512 and 3490 cm<sup>-1</sup>, respectively. The symmetric and asymmetric B-N-B ring modes are predicted at 1340 and 1424 cm<sup>-1</sup>. The in and out of plane scissoring modes are computed at around 900 cm<sup>-1</sup>. These four main bands are effected by the metal ion interactions. The band positions for borazine and M<sup>+</sup>-borazine complexes are listed in Table 2. While N-H

stretches are red-shifted, B-H stretches are predicted to appear at slightly higher frequencies for M<sup>+</sup>-borazine complexes. For Al<sup>+</sup>- and Mn<sup>+</sup>-borazine complexes, all B-H and N-H stretches are equivalent and observed as single peaks. For V<sup>+</sup>-borazine, N-H stretches show a doublet band structure. Because of the back bonding from the two N closer to V, N-H bonds are weaker than the other N-H bond farther from the metal. As a result, two different N-H stretches are predicted. The doublet structure in the N-H stretch region is more pronounced in Zn<sup>+</sup>-borazine, where Zn<sup>+</sup> directly binds to N. B-H stretches are shifted to higher frequencies because the interaction between B and the metal cation induces a partial positive charge on B making B-H bonds stronger. In the far infrared region, the B-N-B ring modes for  $\pi$ -systems (Al<sup>+</sup> and Mn<sup>+</sup>-borazine) shows a doublet feature. On the other hand, due to a greater interaction between M<sup>+</sup> to B and N (for V+

and Zn<sup>+</sup>) B-N-B ring modes turn on showing triplet features in the 1300-1400 cm<sup>-1</sup> region.

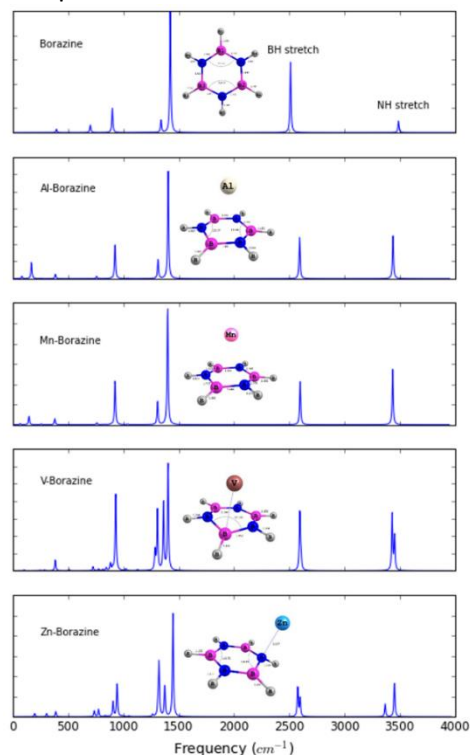


**Figure 3.** Highest occupied molecular orbital (HOMO) (left) and lowest unoccupied molecular orbital (LUMO) (right) of Al<sup>+</sup>-Borazine (upper trace), V<sup>+</sup>-Borazine (middle trace), and Zn<sup>+</sup>-Borazine (lower trace).

## Conclusions

We have studied metal-cation-borazine complexes using density functional theory and 6-311+ G (d, p) basis set. A group III metal (Al) with in empty *d*-orbital, and three transition metals (V, Mn, Zn) with different *d*-electron configuration are chosen to gain an insight into structure and bonding. Al<sup>+</sup> and Mn<sup>+</sup> show a cation- $\pi$  structure with reduced electron donation from the cation. This makes sense because of low electron density on Al, and a half-filled *d*<sup>5</sup> configuration of Mn<sup>+</sup>. A partially filled *d*-orbital in V<sup>+</sup> can undergo *d* $\pi$ -*p* $\pi$  interactions with one of the B atoms in the borazine ring, and therefore V<sup>+</sup> prefers to bind to B in the V<sup>+</sup>-borazine complex. The electrostatic interaction between the Zn cation and the lone pair of N is prominent in Zn<sup>+</sup>-borazine. The structure also shows an increased interaction between B-based *p*-orbital and Zn-based *d*-orbitals. The infrared spectrum of borazine

consists of N-H, B-H stretches and B-N-B ring nodes. These bands remain almost unchanged in Al<sup>+</sup> and Mn<sup>+</sup>-borazine. For V<sup>+</sup>-borazine, a doublet pattern of N-H stretch is predicted for two kinds of stretches: one closer to metal and the other farther from it. Since Zn<sup>+</sup> directly binds to N, these stretches are further apart in the Zn<sup>+</sup>-borazine complex.



**Figure 4.** Infrared spectra of borazine and M<sup>+</sup>-Borazine complexes. The structures are shown in insets.

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