Structural and Electronic Properties of Single-Atom Transition Metal-Doped Boron Clusters MB$_{24}$ (M = Sc, V, and Mn)

Yue-Ju Yang, Shi-Xiong Li,* De-Liang Chen, and Zheng-Wen Long

ABSTRACT: A theoretical study of geometrical structures, electronic properties, and spectral properties of single-atom transition metal-doped boron clusters MB$_{24}$ (M = Sc, V, and Mn) is performed using the CALYPSO approach for the global minimum search, followed by density functional theory calculations. The global minima obtained for the VB$_{24}$ and MnB$_{24}$ clusters correspond to cage structures. Interestingly, the global minima obtained for the ScB$_{24}$ cluster tend to a three-ring tubular structure. Population analyses and valence electron density analyses reveal that partial electrons on transition-metal atoms transfer to boron atoms. The localized orbital locator of MB$_{24}$ (M = Sc, V, and Mn) indicates that the electron delocalization of ScB$_{24}$ is stronger than that of VB$_{24}$ and MnB$_{24}$, and there is no obvious covalent bond between doped metals and B atoms. The spin density and spin population analyses reveal that MB$_{24}$ (M = Sc, V, and Mn) have different spin characteristics which are expected to lead to interesting magnetic properties and potential applications in molecular devices. The calculated spectra indicate that MB$_{24}$ (M = Sc, V, and Mn) has meaningful characteristic peaks that can be compared with future experimental values and provide a theoretical basis for the identification and confirmation of these single-atom transition metal-doped boron clusters. Our work enriches the database of geometrical structures of doped boron clusters and can provide an insight into new doped boron clusters.

1. INTRODUCTION

With the development of science and technology, modern manufacturing technology is moving toward smaller scales. For example, the current semiconductor process has reached the nanometer level. If design and manufacturing can be conducted at the atomic scale, the bottleneck of semiconductor design and manufacturing is expected to be removed and potentially produce disruptive new materials and devices. Clusters are special structures situated between atoms, molecules, and bulk and have different properties compared with bulk materials. For example, the emergence of fullerene C$_{60}$ is a new breakthrough in nanomaterial and nanotechnology, and the discovery of carbon nanotubes and graphene promoted carbon nanomaterials to become a vibrant scientific field. The physical properties of clusters are dependent on their size and shape, which can be changed to give them different physical properties owing to the quantum effect of electrons. Theoretical study of the structure and physical properties of clusters can provide guidance for the design and manufacture of new materials and new devices at the atomic level. Boron is a close neighbor of carbon, and scientists have also conducted extensive research on boron clusters. Boron atoms, with only three valence electrons (one less than carbon), can form polycentric chemical bonds and produce several interesting structures and properties.

Experimental studies have found that anionic pure boron clusters, B$_{n}^{-}$, with less than 38 atoms have a planar or quasi-planar structure.$^{10,11}$ Theoretical studies have found that neutral pure boron clusters of different sizes of B$_{n}$ have planar, tubular, cage-like, or other three-dimensional structures.$^{4,8,12-14}$ In 2014, the breakthrough discovery of borospherene B$_{40}^{-}$ produced a lot of research on boron clusters.$^{15}$ Similar to fullerenes or carbon nanotubes, boron clusters may be used as molecular devices. Various chemical modifications are carried out to form boron-based nanomaterials with novel structures.

Similar to fullerenes, doping of metal atoms into boron clusters can produce new structures or properties.$^{18,20-22,25-38}$ For example, in the case of an alkali metal, experimental research combined with theoretical calculation revealed that B$_{20}^{-}$, B$_{22}^{-}$, and B$_{24}$ have a quasi-planar structure, quasi-planar structure, and double-ring tubular structure, respectively.
However, both LiB$_{20}^-$ and MB$_{22}^-$ (M = Na and K) possess a double-ring tubular structure and Li$_2$B$_{24}$ possesses a three-ring tubular structure. In addition, Li-, Na-, or K-doped borospherene B$_{40}$ is expected to become a nonlinear optical (NLO) nanomaterial. Because of their rich electronic structure characteristics, transition metals can combine with boron clusters to produce rich structures and properties. For example, the quasi-planar B$_{12}$ cluster has a semisandwich structure after being doped with metal atoms such as Co and Rh. Neutral B$_{24}$ has a double-ring tubular structure, while TiB$_{24}$ and CrB$_{24}$ have a cage structure after doping with one Ti or Cr atom. The single-atom Sc- or Ti-doped borospherene B$_{40}$ is expected to become a hydrogen-storage material. In addition, Li-, Na-, or K-doped borospherene B$_{40}$ is expected to become a nonlinear optical (NLO) nanomaterial. Because of their rich electronic structure characteristics, transition metals can combine with boron clusters to produce rich structures and properties. For example, the quasi-planar B$_{12}$ cluster has a semisandwich structure after being doped with metal atoms such as Co and Rh. Neutral B$_{24}$ has a double-ring tubular structure, while TiB$_{24}$ and CrB$_{24}$ have a cage structure after doping with one Ti or Cr atom. The single-atom Sc- or Ti-doped borospherene B$_{40}$ is expected to become a hydrogen-storage material.

2. COMPUTATIONAL METHODS

Geometric structure searches of neutral MB$_{24}$ (M = Sc, V, and Mn) clusters were implemented using particle swarm optimization (CALYPSO) software. CALYPSO is a powerful cluster structure search method, which has been successfully applied to boron and doped boron clusters. In addition, Li-, Na-, or K-doped borospherene B$_{40}$ is expected to become a nonlinear optical (NLO) nanomaterial. Because of their rich electronic structure characteristics, transition metals can combine with boron clusters to produce rich structures and properties.

Figure 1. Structures of doped boron clusters ScB$_{24}$. Values in parentheses are the relative energies (eV) of the five low-energy isomers for ScB$_{24}$ at the PBE0/def2-TZVP level. Values in square brackets are the relative energies (eV) of the five low-energy isomers for ScB$_{24}$ at the PBE0/6-311G* level. The top row is the side view and the bottom row is the top view. (a) I $D_{2d}$ (b) II $C_2$ (c) III $C_1$; (d) IV $C_2$; and (e) V $C_{2h}$.

Figure 2. Structures of doped boron clusters VB$_{24}$. Values in parentheses are the relative energies (eV) of the five low-energy isomers for VB$_{24}$ at the PBE0/def2-TZVP level. Values in square brackets are the relative energies (eV) of the five low-energy isomers for VB$_{24}$ at the PBE0/6-311G* level. The top row is the side view and the bottom row is the top view. (a) I $D_3$; (b) II $C_{2h}$; (c) III $C_2$; (d) IV $C_s$; and (e) V $C_{2h}$.
Figure 3. Structures of doped boron clusters MnB24. Values in parentheses are the relative energies (eV) of the five low-energy isomers for MnB24 at the PBE0/def2-TZVP level. Values in square brackets are relative energies (eV) of the five low-energy isomers for MnB24 at the PBE0/6-311G* level. The top row is the side view and the bottom row is the top view. (a) I C2h; (b) II C2v; (c) III C4v; (d) IV C2v; and (e) V D2h.

Table 1. Lowest Frequencies, Average Binding Energy, Charges on the Doped Atom, Dipole Moments (μ), and Mayer Bond Orders between Doped Metal Atoms and B Atoms of MB24 (M = Sc, V, and Mn)

| Cluster    | Lowest frequencies/cm⁻¹ | Average binding energy/eV | Charges on doped atom | μ (debye) | Mayer bond order between doped atom M and B atom |
|------------|--------------------------|---------------------------|-----------------------|----------|-----------------------------------------------|
| ScB24      | 156                      | 5.31                      | 0.50                  | 0        | 0.14–0.19                                     |
| VB24       | 73                       | 5.39                      | 0.80                  | 0        | 0.17–0.22                                     |
| MnB24      | 135                      | 5.31                      | 0.97                  | 0.1      | 0.08–0.24                                     |

length (2.77) of V−V obtained by Langridge-Smith et al.\(^52\) Therefore, the discussion below is on the basis of the PBE0/6-311G* level. All computations were performed using Gaussian 16 software.\(^53\) All analyses and various types of isosurface map drawings were realized using the Multiwfn 3.7(dev) code.\(^54\)

### 3. RESULTS AND DISCUSSION

#### 3.1. Structures and Electronic Properties

The five low-energy structures of transition metal-doped boron clusters MB24 (M = Sc, V, and Mn) are shown in Figures 1–3. The calculation results show that the low-energy structures of MB24 (M = Sc, V, and Mn) tend to form cage structures, and the lowest-energy structures of MB24 (M = Sc, V, and Mn) are characterized by the lowest spin multiplicity (doublet). Early research found that B24 has a double-ring tubular structure, and B24− has a planar structure. It can be seen from Figure 1 and the calculation results that after adding Sc atoms, the lowest energy structure I of ScB24 has a three-ring tubular structure, comprising three eight-membered rings. The lowest energy structure I has high symmetry (D₈h), and the Sc atom is located at the center of the tube. The distance between the Sc atom and each B atom on the eight-membered rings at both ends is 2.59 Å, and the distance from the Sc atom to each B atom on the middle-eight-membered ring is 2.30 Å. Similar to tubular B clusters, Sc-doped boron clusters are expected to become the basic unit of boron nanotube materials, which will be further synthesized into boron nanotubes.

It can be seen from Figures 2 and 3 that the lowest energy structures of VB24 and MnB24 have similar cage structures comprising a six-membered ring at each end and two six-membered rings in the middle. Among them, VB24 has high symmetry (D₆h), and the V atom is located at the center of the cage. The distance between the V atom and each B atom on the six-membered rings at each end of the cage is 2.54 Å, and the distance between the V atom and each B atom on the two six-membered rings in the middle is 2.40 Å. The Mn atom of MnB24 slightly deviates from the center of the cage, which leads to a decrease in the symmetry of MnB24 (C₈). In the following discussion, the main focus is on the study of the lowest energy structure I.

Some of the ground-state parameters of transition metal-doped boron clusters MB24 (M = Sc, V, and Mn) are listed in Table 1, including the lowest harmonic frequency, dipole moment, atomic charge on doped transition-metal atoms, and Mayer bond level.\(^55\) The lowest harmonic frequency analysis (see Table 1 for the lowest harmonic frequencies of each cluster) confirmed that these lowest energy structures are indeed stable (no imaginary frequency). To further illustrate the stability of the clusters, the average binding energy of the clusters is calculated, as follows

\[
E_b(MB_{24}) = [nE(B) + E(M) - E(MB_{24})]/(n + 1) \tag{1}
\]

The calculation results are listed in Table 1. The average binding energy of MB24 (M = Sc, V, and Mn) is approximately 5.3 eV, indicating that the stabilities of MB24 (M = Sc, V, and Mn) are not much different.

The charge population analysis shows that all the metal atoms show positive charges, indicating that electrons have been transferred to the boron atoms and the Mn atoms have transferred almost one electron. Because there is more than one outer valence electron of Sc, V, or Mn, only a small part of the electrons has been transferred. Analysis shows that the Mayer bond level of the metal atom M and B atom of these clusters is between 0.08 and 0.24 and it is less than 1, indicating that no obvious covalent bond is formed between the metal atom and the B atom. Because ScB24 and VB24 have high symmetry, D₈h and D₆h, their dipole moments are 0. MnB24 exhibits a small dipole moment owing to its reduced symmetry, although its structure is similar to that of VB24.

Figures 4 and S1 and S2 (Supporting Information) show the localized orbital locator (LOL)\(^56\) of the valence electrons of ScB24, VB24, and MnB24. The LOL can well-describe the
disconnected at both ends of the tube (see the isosurface connected on the tube wall but the isosurface map is maps of ScB24 are connected on the tube wall and the isosurface value is 0.59 (data not shown), the isosurface value, the whole ScB24 molecule is stronger than that of the other two clusters. Tubular-structure ScB24 and cage-type VB24 and MnB24 are expected to become the basic units of boron nanomaterials and be further synthesized into boron nanotubes or other three-dimensional materials. Considering the electron delocalization characteristics of these clusters, they are expected to be applied to molecular devices or molecular switches.

To further characterize the electron localization and chemical bonds, the electron localization function (ELF)57 of the valence electrons was analyzed, as shown in Figures S3–S5 (Supporting Information). Figures S3–S5 also show that there is a wide blank area around the metal atom, showing that the metal atom does not form an obvious covalent bond with the surrounding B atoms, which is consistent with the Mayer bond level and LOL analysis. In addition, with the increase in the isosurface value, the ELF isosurface shows similar characteristics to the LOL isosurface such as the delocalization of whole ScB24 molecule is stronger than that of the other two clusters. Figures S6 and S7 (Supporting Information) show the isosurface diagrams of valence electron density for ScB24, VB24, and MnB24 with isosurface values of 0.16 and 0.20, respectively. Electron density describes the characteristics of electron distribution. Under the same isosurface value, a fatter (represents the bigger volume and wider connected area occupied by an isosurface map) isosurface means more electrons and a thinner isosurface means fewer electrons. The isosurface diagram of Sc is the thinnest and that of Mn is the thickest under the same isosurface value, indicating that the electron density of Mn is the highest. From the previous atomic charge population analysis, we found that the charges on Sc, V, and Mn were 0.5, 0.8, and 0.97, respectively. The valence electrons of Sc, V, and Mn are 3, 5, and 7, respectively, so when the transferred electrons are removed, the remaining valence electrons of Sc, V, and Mn should be 2.5, 4.2, and 6.03. From this, it can be inferred that under the same isosurface value, the isosurface map of the Mn atom is the thickest and that of Sc is the thinnest. In addition, because the B atom has three valence electrons in addition to part of the electrons transferred from the metal atom, it has between 3 and 4 valence electrons. Therefore, the electron density of the B atom should be greater than that of Sc but less than that of V and Mn. The calculation results (isosurface diagrams of valence electron density) show that as the value of the isosurface increases, the isosurface diagram of the Sc atom will disappear first and that of the B atoms in the ScB24 will disappear later (as shown in Figures S6a and S7a), indicating that the electron density of the B atoms is greater than that of Sc. With the increase in the isosurface value, the isosurface diagrams of the B atoms in VB24 and MnB24 will disappear first, and the electron density isosurfaces of V and Mn atoms will disappear later, indicating that the electron density of the B atoms is less than those of the V and Mn atoms. The electron density isosurface diagrams are qualitatively consistent with the atomic charge analysis results.

Figure 5 shows the isosurface diagram of the spin density of ScB24, VB24, and MnB24. Spin density reveals the distribution of unpaired electrons (single electrons) in three-dimensional
electron in the ScB$_{24}$ system, of which 0.38 is on the Sc atom and the remaining 0.62 is on the B atom. This result is consistent with the spin density diagram. The VB$_{24}$ system has one unpaired single $\alpha$ electron, of which 0.97 is on the V atom and the remaining 0.03 is on the B atom (this basically can be ignored). This result is also consistent with the spin density diagram. Although the total number of unpaired electrons in the MnB$_{24}$ system is 1, 2.01 unpaired $\alpha$ electrons and 1.01 unpaired $\beta$ electrons are distributed in the system, of which 1.83 $\alpha$ electrons are on the Mn atom and 0.18 $\alpha$ electrons are on the two B atoms; the 1.01 $\beta$ electrons are distributed on the remaining B atoms. This result is also consistent with the spin density diagram. The spin density reflects chemical reactions or adsorption to a certain extent. The single electrons of ScB$_{24}$ are all $\alpha$ electrons and are basically evenly distributed on the B atoms. The B atoms containing $\alpha$ single electrons can pair with free radicals or small molecules containing $\beta$ single electrons to form new covalent bonds. For the MnB$_{24}$ system, two B atoms with single $\alpha$ electrons can adsorb or react with free radicals or small molecules with single $\beta$ electrons, while B atoms with single $\beta$ electrons can adsorb or react with atoms, free radicals, or small molecules with $\alpha$ single electrons. In addition, these spin features are expected to produce interesting magnetic properties, which will further lead to potential applications in molecular devices.

### 3.2. Polarization Properties

To understand the polarization properties of the clusters, the polarizability of the system was calculated, including average isotropic polarizability $\alpha$, average polarizability $\bar{\alpha}$ of a single atom, anisotropic polarizability $\Delta \alpha$, and the first hyperpolarization $\beta_0$. $\alpha$ is also called the linear optical coefficient. The anisotropic polarizability describes the response of the system to electric fields from different directions. The larger the value, the stronger is the anisotropic response to the external electric field. The first hyperpolarizability is also called the second-order NLO coefficient, which evaluates the NLO properties of molecules. It can be seen from Table 2 that the polarizability of ScB$_{24}$ is slightly higher than that of VB$_{24}$ and MnB$_{24}$ indicating that the bonding interactions between the atoms within ScB$_{24}$ are slightly stronger than those of VB$_{24}$ and MnB$_{24}$, and ScB$_{24}$ is more likely to be polarized by an external electric field. The average polarizability of ScB$_{24}$ is slightly greater than that of VB$_{24}$ and MnB$_{24}$, indicating that the electronic structures of VB$_{24}$ and MnB$_{24}$ are relatively stable. The anisotropic polarizability of VB$_{24}$ is the smallest and that of ScB$_{24}$ is the largest, indicating that VB$_{24}$ has the weakest anisotropic response and ScB$_{24}$ has the strongest response to an external electric field. It can be seen from Table 2 that the first hyperpolarizability of ScB$_{24}$ is equal to 0, indicating that there is no NLO response; the first hyperpolarizability of VB$_{24}$ is 0.436, indicating that the NLO response is extremely small, and MnB$_{24}$ has a larger first hyperpolarizability, indicating that MnB$_{24}$ has a strong NLO response.

### 3.3. Infrared and Raman Spectra

Figures 6 and 7 show plots of the calculated infrared and Raman spectra of MB$_{24}$ (M

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**Table 2. Polarizabilities of MB$_{24}$ (M = Sc, V, and Mn)**

|      | $\alpha$/au | $\bar{\alpha}$/au | $\Delta \alpha$/au | $\beta_0$/au |
|------|-------------|-------------------|--------------------|-------------|
| ScB$_{24}$ | 299.047     | 11.96             | 27.29              | 0           |
| VB$_{24}$  | 280.658     | 11.22             | 12.59              | 0.436       |
| MnB$_{24}$ | 284.329     | 11.37             | 19.91              | 53.83       |
Among the 69 vibration modes of ScB$_{24}$, only 13 modes are vibration. From the calculation results, it can be seen that the arrangement of atoms will lead to different stretching or bending vibrations of the atoms. The frequency because these vibration modes are derived from the cluster structure has a strong influence on the harmonic frequency because these vibration modes are derived from the stretching or bending vibrations of the atoms. Differences in the arrangement of atoms will lead to different modes of vibration. From the calculation results, it can be seen that among the 69 vibration modes of ScB$_{24}$, only 13 modes are infrared-active and 56 are all inactive. Among the 13 infrared-active modes, five pairs are double-degenerate vibration modes, so there are eight infrared peaks. In the infrared spectrum of ScB$_{24}$, the first and second peaks are located at 278 and 419 cm$^{-1}$, respectively, and the second peak is produced by a pair of degenerate vibration modes. The third peak is the strongest, located at 457 cm$^{-1}$, and is generated by a pair of degenerate vibration modes (in Figure S8a,b). The thick yellow arrow in Figure S8 is the direction vector of the dipole moment changes caused by the vibration (under resonance approximations, only the infrared intensity of the mode whose dipole moment changes is not zero). The fourth to eighth peaks are located at 592, 669, 731, 813, and 857 cm$^{-1}$, respectively. The eighth peak is not shown in the figure owing to its weak activity. The fifth, sixth, or eighth peak was generated by a pair of degenerate vibration modes. Among the 69 vibration modes of ScB$_{24}$, 19 modes are Raman-active vibration modes and 50 are inactive modes. Among the 19 Raman-active modes, eight pairs are degenerate vibration modes. The strongest peak is located at 613 cm$^{-1}$ and is generated by the radial breathing vibration of the boron atoms on the ring (the vibration mode is shown in Figure S8c). This radial breathing mode can reveal important characteristics of nanotubes. It can be seen from the calculation results that the 13 infrared-active modes are Raman-inactive and the 19 Raman-active modes are all infrared-inactive. Under the resonance approximation, the infrared intensity is not zero for only the mode where vibration changes the dipole moment and the Raman activity is not zero for only the mode where vibration changes the polarizability. Therefore, the 13 infrared-active modes did not cause changes in the polarizability and the 19 Raman-active modes did not cause changes in the dipole moment. These vibration characteristics are mainly due to the three-ring structure of ScB$_{24}$ and the high $D_{6h}$ symmetry.

The calculation results show that among the 69 vibration modes of VB$_{24}$, 41 modes are infrared-active vibration modes and 28 are inactive modes. The strongest infrared peak is also a pair of degenerate vibration modes (the vibration mode is shown in Figure S8d,e). Among the 69 vibration modes of VB$_{24}$, there are 57 Raman-active modes and 12 inactive modes. The strongest Raman peak is located at 622 cm$^{-1}$, which is also produced by the radial breathing vibration of boron atoms (the vibration mode is shown in Figure S8f). Among the 69 vibration modes of MnB$_{24}$, 59 are infrared-active and 10 are inactive. The vibration mode of the strongest infrared peak is shown in Figure S8g. The 69 vibration modes of MnB$_{24}$ are Raman-active modes, and the strongest Raman peak is located at 614 cm$^{-1}$. This strongest peak is also generated by the radial breathing vibration of boron atoms (the vibration mode is shown in Figure S8h). It can be seen from Figure 6 that VB$_{24}$ and MnB$_{24}$ have some similar band characteristics, but owing to the low symmetry of MnB$_{24}$, many new band characteristics are also generated, such as several stronger peaks around 200 cm$^{-1}$. In addition, from Figure 7 and the calculation results, the strongest Raman peaks of the three structures are all located at approximately 610 cm$^{-1}$, and they are all radial breathing modes. Although VB$_{24}$ and MnB$_{24}$ have cage structures, they can be considered variable-diameter tubes. The diameters of the rings are approximately 3.5 Å; therefore, the breathing mode of the three structures is located at approximately 610 cm$^{-1}$. The characteristic peaks and band characteristics of the clusters can be used to identify these structures, which can be compared and analyzed in future experiments.

### 3.4. Electronic Absorption Spectra

Based on the previous calculations, the TD-PBE0/6-311G$^*$ method was used to calculate the ultraviolet (UV)–visible spectrum of
MB₄₄ (M = Sc, V, and Mn) (excitation energy E, wavelength λ, and oscillator intensity f of the first 36 excited states). Figure 8

![Electronic absorption spectra](https://doi.org/10.1021/acsomega.1c03740)

**Figure 8.** Electronic absorption spectra. The black line represents ScB₂₄, the blue line represents VB₂₄, and the red line represents MnB₂₄.

| M     | wavelength of the first excited state (oscillator intensity) | first absorption peak (corresponding excited states) |
|-------|-----------------------------------------------------------|--------------------------------------------------|
| ScB₂₄ | 1110 nm (0)                                               | 474 nm (30)                                      |
| VB₂₄  | 1984 nm (0)                                               | 1319 nm (3,4)                                   |
| MnB₂₄ | 3302 nm (0.0001)                                          | 3302 nm (1)                                     |

shows the electronic absorption spectra, and Table 3 shows some of the excited-state parameters. It can be seen from Table 3 that except for ScB₂₄, the absorption peaks of these clusters extend to the infrared band. The wavelength of the first excited state of MB₂₄ (M = Sc, V, and Mn) is in the infrared band, and the first excited state of ScB₂₄ and VB₂₄ is the forbidden excited state (oscillator intensity is 0) (see Table 3). The first excited states of ScB₂₄, VB₂₄, and MnB₂₄ are mainly derived from the electronic transitions of β-HOMO → β-LUMO, β-HOMO → β-LUMO, and α-HOMO → α-LUMO, respectively. In addition, it can be concluded from Table 3 that the wavelength of the first excited state of MnB₂₄ (3302 nm) is the largest, the wavelength of the first excited state of VB₂₄ is 1984 nm, and the wavelength of the first excited state of ScB₂₄ (1110 nm) is the shortest. Although the structures of VB₂₄ and MnB₂₄ are similar, their excitation characteristics are obviously different.

From Figure 8 and Table 3, it can be seen that only the first absorption peak of ScB₂₄ is in the visible light band and the first absorption peaks of VB₂₄ and MnB₂₄ are both in the infrared light band. The first absorption peak of MnB₂₄ in the main picture of Figure 8 is too weak to be displayed (see the inset for the enlarged absorption peak), which is located at 3302 nm. It can be seen from Table 3 that only the first absorption peak of MnB₂₄ corresponds to the wavelength position of the first excited state, and the absorption is very weak. However, because the first and second excited states are forbidden excited states, the first absorption peak of VB₂₄ corresponds to the wavelength (1319 nm) of the third and fourth excited states (degenerate). In particular, there is only one absorption peak in the UV-visible spectrum of ScB₂₄, which is derived from the 30th excited state (wavelength is 474 nm), and the other excited states are forbidden excited states. The 30th excited state comes from the electronic transition of α-HOMO → α-LUMO + 7. The electron absorbs the photon to transition from the ground state to the excited state when the vibration transition is not zero, then transitions from the highly excited state to the low excited state (nonradiative transition), and finally transitions from the lowest excited state back to the ground state and emits light. From the foregoing analysis, it can be inferred that the wavelengths corresponding to the first excited state of these clusters returning to the ground state are all in the infrared light region, so there are emission spectra in the infrared light band. The spectral characteristics of these clusters can be used to identify their structures.

### 4. CONCLUSIONS

In this work, density functional theory combined with the particle swarm optimization algorithm (CALYPSO) software is used to research the ground-state geometric structure of transition metal-doped boron clusters MB₂₄ (M = Sc, V, and Mn). The electronic structures and spectral properties such as infrared and Raman spectra are further discussed. Research results include the following seven points: (1) ScB₂₄ has a three-ring tubular structure, while VB₂₄ and MnB₂₄ have cage structures. (2) Charge population analysis and valence electron density analysis show that doped atoms transfer part of their electrons to boron atoms. (3) The LOL analysis shows that the electron delocalization effect of the entire ScB₂₄ molecule is greater than that of VB₂₄ and MnB₂₄; however, the metal atoms and the surrounding B atoms do not form an obvious covalent bond. (4) The electron spin density analysis shows that ScB₂₄ can adsorb free radicals or small molecules with β single electrons. For the MnB₂₄ system, two B atoms with single electrons can adsorb free radicals or small molecules with β single electrons or react with free radicals or small molecules with β single electrons; B atoms with β single electrons can adsorb atoms, free radicals, or small molecules with α single electrons or react with atoms, free radicals, or small molecules with α single electrons. (5) The polarization analysis indicates that the average polarization of each atom of ScB₂₄ is greater than that of VB₂₄ and MnB₂₄. The first hyperpolarization of ScB₂₄ is 0, which indicates that there is no NLO response. (6) The infrared and Raman spectroscopies show that ScB₂₄ has eight infrared-active characteristic peaks. The strongest Raman-active modes of ScB₂₄, VB₂₄, and MnB₂₄ are located at approximately 610 cm⁻¹. These characteristics can be compared with the experimental values. (7) Through the analysis of the electronic absorption spectra of the clusters, ScB₂₄ is found to have the only strong absorption peak in the visible light region, and VB₂₄ and MnB₂₄ have weaker absorption peaks in the infrared light region. This research has enriched the structure of doped boron clusters and has certain theoretical guiding significance for the preparation of new boron nanomaterials, especially boron nanotubes.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03740.

- LOL of MB32 (M = Sc, V, and Mn); ELF of MB34 (M = Sc, V, and Mn); valence electron density of MB34 (M = Sc, V, and Mn); and vibrational modes of MB34 (M = Sc, V, and Mn) (PDF)

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Notes
The authors declare no competing financial interest.

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