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Global Minimum Search for the Largest Ge Cage Stabilized by a Single Interstitial Metal Atom

Alexis Kiefer
amk308@uakron.edu

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Honors Project Research Project- Executive Summary

Dr. Ivan Popov

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Introduction

In recent years, clusters have been heavily researched and analyzed with investigation into structures being the bulk of these studies for both computational and experimental methods.[1,2] Clusters are known as the state between atoms and bulk materials, which offer different properties that can be useful.[3] The conformations of clusters offer nearly an indefinite number of structural makeups that each offer their own electrochemical and bonding properties. Clusters offer development and advancement of novel materials by fitting specific chemical and physical properties that are needed for materials of many different purposes. The most valuable finding from metal cluster research is the global minimum structure that is formed from computational or theoretical methods.[4,5] The global minimum is the most stable conformation that the metal cluster creates and is most likely to be synthesized through experimental efforts. There are different stable conformations, called local minima, but the global minimum is sought after.

Metal clusters have been extensively researched using germanium atoms with interstitial transitions metals.[6,7] The intention of these theoretical efforts was to find the global minimum structure of $[M_y@Ge_x]^z$ from a given amount of Ge atoms (x) and a given amount (y) of interstitial metal atom (M) with a charge (z) as a closed cage structure. These reported structures have the Ge atoms in a cage conformation that are completely encapsulating the metal atom. Different numbers of Ge atoms and interstitial metal atoms were found and reported to make caged structures.[8-13] The novel research of the $[M@Ge_{15}]^x$ stabilized by one interstitial metal atom was the sole research focus.

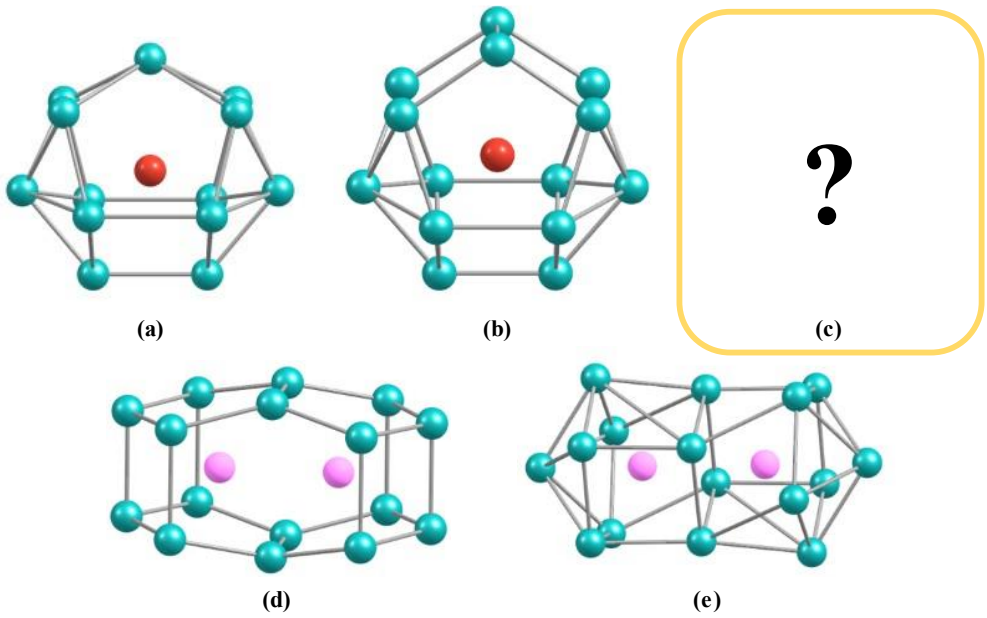

Figure 1. Selected examples of single/double closed-cage systems. $[Nb@Ge_{13}]^{3-}$ (**a**)[1], $[Nb@Ge_{14}]^{3-}$ (**b**)[1], possible $[M@Ge_{15}]^{x}$ (**c**), α-$[Co_2@Ge_{16}]^{4-}$ (**d**)[2], and β-$[Co_2@Ge_{16}]^{4-}$ (**e**)[2].

Research regarding clusters with either one less or more Ge atom from Ge_{15}, Ge_{14} and Ge_{16}, was theorized and analyzed. All findings are considering if the metal atom will stabilize the cluster and in turn create a cage structure. Large transition metals are used because of the large possible orbital overlap that occurs from stabilizing the cage. The $[Nb@Ge_{14}]^{3-}$ computational findings showed a closed-cage structure that was created to make and stabilize an endohedral Ge cluster with 14-vertices[1] (**Figure 1b**). These same findings found that $[Nb@Ge_{13}]^{3-}$ cluster stabilized a cage with 13-vertices[1] (**Figure 1a**). Comparable research to Ge_{14} clusters has been performed on Ge_{13} clusters. $M@Ge_{13}$ research suggests that transition metals that can support the Ge_{13} cages, with the lowest energy, are found to be either capping of hexagonal prism or antiprism as their formed cluster structure.[3] Ge_{16} had quite different findings due to the cluster size increase, which gave rise to the problem of stabilizing a cluster using just one interstitial transition metals.[3] Theoretical methods found that two interstitial metal atoms are used to stabilize the Ge_{16} cage.[2] The two-metal cage structure, $[Co_2@Ge_{16}]^{4-}$, conformed to a stabilized cage that looked like a capsulate, the α-form, or double cage structure, β-form[2] (**Figure 1d & 1e**).

The Ge_{15} research was focused on finding a metal that could form a closed-cage structure. The Coalescence Kick program[14] was used to create a different set of structures for each tested metal. The ordering of the structures ranked from lowest to highest was contained in an output file, "analysis.out", according to their Gibbs free energy for each cage. Analyses of the lowest relative energy conformations to 30 kcal/mol were conducted to find each unique structure for each interstitial metal. A compilation of these structures was ordered from lowest to highest energy with the respective point group, spectroscopic state, and relative energy in a table, starting at the global minimum. A cluster was found to create the closed-cage structure as a global minimum conformation with a single transition metal atom. More intensive computational

research was performed on the closed-cage cluster with one metal atom to provide more descriptive and conclusive results.

Computational Methods

Computational methods were used to create and theoretically prove if the Ge_{15} cage can be stabilized with each single interstitial transition metal used. In various theoretical investigations on Ge clusters, various methods and basis sets were used for computational calculations.[3]

The Coalescence Kick program produced all the structures that are found for all the Ge_{15} clusters that were reported. From the Coalescence Kick program, 25,000 structures were generated and optimized. From there, the top 50 lowest energy structures were selected. Then, these structures were optimized using more robust calculations to provide a more accurate ranking. To obtain their ranking, the "analysis.out" file was used, which orders structures by their relative energies. From this file, the structures that had energies less than 30 kcal/mol were inspected for imaginary frequencies, point group, and spectroscopic state. Recalculations were done to optimize a structure that was close to conforming to a point group. The top structures up to 30 kcal/mol for each transition metals were reflected in their own tables.

The resulting findings called for further theoretical exploration to be run on the top 10 structures on the true finding of the global minimum structure. Further calculations were run to determine and validate that the global minimum structure obtained from the original method was still the lowest in energy using a different method.

The closed-cage global minimum structure was then investigated by the Adaptive Natural Density Partitioning method (AdNDP). This program uses the Lewis theory and canonical molecular orbital theory to describe the chemical bonding by finding electron pair localizations.[15] The total valence electrons from the global minimum cluster were totaled to find the number of bonds.

Conclusion

DFT calculations were used to find the ranking of the optimized top 30 kcal/mol structures produced from the Coalescence Kick calculated structures for transition metals. It has been found that a Ge_{15} cage can be successfully stabilized by a single, interstitial metal atom. The global minimum structure was validated using more robust calculations. The average M-Ge bonds and the Ge-Ge bonds of the global minimum cluster were longer than the sum of the covalent radii, thus suggesting that electron delocalization is present in the cluster. Substantial chemical bonding analysis uncovered that in the global minimum cluster there are 1c-2e, 3c-2e, and 4c-2e interactions. The ideal ON is 2.00 |e|, but this was not seen for each set of interactions. Less than the ideal ON was discovered ranging between 1.80-1.88 |e| for 1c-2e, 1.88 |e| for 3c-2e, and 1.90-1.93 |e| for 4c-2e. Other larger covalent radius transition metal atoms could be used for future calculations to find if more can stabilize the Ge_{15} cage. Furthermore, experimentalists will now be able to use this data to start the experimentation process of the found cluster.

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