CME LIVE OPEN ACCESS

Journal of
Theoretical Physics & Mathematics Research

Short Research

ISSN: 3065-8802

Stability and Reactivity of Double Icosahedron $Ag_{17}M_2$ (M=Ni, Cu, Zn) Clusters

P. L. Rodríguez-Kessler *

Centro de Investigaciones en Óptica A.C., Loma del Bosque 115,
Lomas del Campestre, León, 37150, Guanajuato, México.

Corresponding Author: P. L. Rodríguez-Kessler, Centro de Investigaciones en Óptica A.C., Loma del Bosque 115, Lomas del Campestre, León, 37150, Guanajuato, México.

Received: 2025 Mar 21 **Accepted:** 2025 Apr 09 **Published:** 2025 Apr 14

Abstract

Herein, the structure and stability of double icosahedron $Ag_{17}M_2$ *(M = Ni, Cu, Zn) clusters are investigated using density functional theory (DFT) computations. The results indicate that the clusters favor endohedral configurations in the doublet state, as confirmed with four different functionals: BP86, PBE0, B3PW91, and TPSSh. Additionally, the doped clusters exhibit higher ionization energies and electronegativities compared those of the bare* Ag_{19} *cluster. After doping, the ELF function increases at the Ag sites, which reveals important implications for catalysis.* .

Keywords: Stability, Nanoclusters, Calculations, Electronic Properties, Catalysis

1. Introduction

Nanoclusters, particularly those composed of noble metals like silver, have drawn considerable attention due to their unique structural, electronic, and catalytic properties. The arrangement of atoms within these clusters often leads to behaviors that deviate from those of bulk materials, making them ideal candidates for a variety of technological applications. Among these, the double icosahedron structure, characterized by a distinct icosahedral geometry with enhanced stability, is a particularly interesting motif in the study of metallic clusters [1-3]. Moreover, clusters of coinage and noble metals have demonstrated enormous potential for electrocatalysis. While noble-metal clusters demonstrate remarkably high catalytic activity in facilitating the four-electron reduction of oxygen molecules, transition metals suffer from corrosion issues under acidic conditions [4]. Silver and its alloys exhibit notable stability and high activity for the oxygen reduction reaction (ORR) under alkaline conditions, making them attractive, low-cost alternatives to noble-metal catalysts [5]. Previous DFT studies have shown that core-shell Ag nanoclusters, especially those with noble-metal cores, are promising catalysts for ORR [6, 7]. The development of noble-metal-free catalysts, such as Ag- based nanoclusters and alloys, is crucial for expanding the range of catalysts suitable for alkaline fuel cell applications. Moreover, small coinage metal clusters showed promising properties for the hydrogen evolution reaction [8]. In this work, we anticipate the stability and reactivity of double icosahedral $Ag_{17}M_2$ clusters, where M represents the transition metals Ni, Cu, and Zn. The results show that the incorporation of two M atoms into the silver framework introduces significant modifications to their stability and reactivity. The structural stability, bonding interactions, and energetic preferences of these systems are investigated by means of density functional theory (DFT). The findings of this study provide crucial insights into the effect of metal substitution on the stability and chemical reactivity of $Ag_{17}M_2$ clusters, highlighting their potential for catalysis and other applications that require enhanced nanomaterial reactivity.

1.1. Computational Details

Calculations performed in this work are carried out by using density functional theory (DFT) as implemented in the ORCA 6.0.0 code [9]. The exchange and correlation energies are addressed by the PBE0 functional in conjunction with the Def2-ECP and auxiliary def2/J basis sets, where ECP stands for effective core potential [10-13]. Atomic positions are self-consistently relaxed through a Quasi-Newton method employing the BFGS algorithm. The SCF convergence criterion is set to Tight SCF in the input file. This results in geometry optimization settings of $1.0e^{-08}$ Eh for total energy change and $2.5e^{-11}$ Eh for the one-electron integrals. The Van der Waals interactions are included in the exchange-correlation functionals with empirical dispersion corrections of Grimme DFT-D3(BJ). The electron localization function (ELF) was computed and analyzed using Multiwfn [14]. Theoretical descriptors such as hardness (η), electronegativity (χ), and electrophilicity index (ω), can be derived from the Koopman's theorem and are used to evaluate the chemical stability of $Ag_{17}M_2$ clusters, which can be obtained by using the following equations:

Citation: Rodríguez-Kessler, P. L. (2025). Stability and Reactivity of Double Icosahedron Ag17M2 (M=Ni, Cu, Zn) Clusters. *J Theor Phys Math, 3* (1), 1-5.

$$\eta = \frac{I - A}{2}, \qquad (1)$$

$$\chi = \frac{I + A}{2}, \qquad (2)$$

$$\omega = \frac{\chi^2}{2\eta}, \qquad (3)$$

where I and A are the vertical ionization energy and vertical electron affinity parameters, which are calculated following previous works [15-18].

2. Results

The $Ag_{17}M_2$ (M = Ni, Cu, Zn) clusters investigated in this work are calculated by using a double icosahedron structure model, as shown in Figure 1. The results show that the clusters favor the endohedral doping over the exohedral configurations, which is also observed for smaller icosahedral clusters. Interestingly for $Ag_{17}Zn_2$ cluster the endohedral configuration is also more favorable than exohedral configurations (Figures 1b, 1c), although the exohedral configuration in the 13-atom icosahedral cluster ($Ag_{12}Zn$) is more stable [19]. Moreover, the low-spin state (doublet) is favored over the quartet state for these clusters, as confirmed by four different functionals (see Table I).

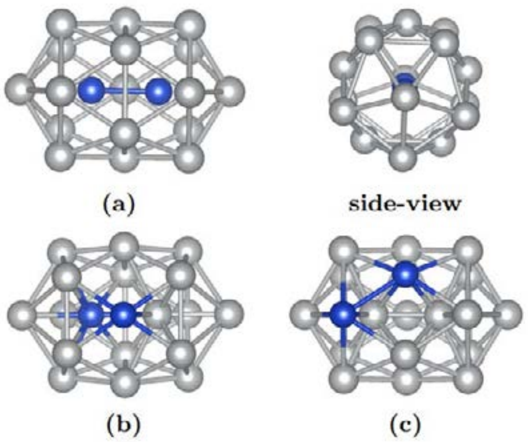

Figure 1: Double Icosahedral Structure Model for Representing $Ag_{17}M_2$ Clusters. Three Different Chemical Orderings (a, b, c) are Used to Represent the Endohedral and Exohedral Configurations.

Label	S_M	BP86	PBE0	B3PW91	TPSSh
$Ag_{17}Ni_2$	2	0.00	0.00	0.00	0.00
$Ag_{17}Cu_2$	2	0.00	0.00	0.00	0.00
$Ag_{17}Zn_2$	2	0.00	0.00	0.00	0.00
$Ag_{17}Ni_2$	4	0.30	0.25	0.07	0.28
$Ag_{17}Cu_2$	4	0.52	0.43	0.45	0.47
$Ag_{17}Zn_2$	4	0.86	0.80	0.83	0.75

Table 1: Relative Energies (in eV) of the Lowest Energy Structures of $Ag_{17}M_2$ (Ni, Cu, Zn) Clusters Computed at Different DFT Levels. Representative Values on the Spin Multiplicity (SM) are Given.

To identify the fingerprints of the clusters, we have calculated their infrared (IR) spectra, which will serve as a reference for future experimental studies [20, 21]. All the clusters show a similar IR spectrum with two main peaks, with the intensity depending on the composition, for example, $Ag_{17}Zn_2$ and Ag_{19} show the first peak as more pronounced than the second one (Figure 2). The characteristic peak for $Ag_{17}M_2$ (M = Ni, Cu, Zn) is found at 190.56, 88.81, and 151.31 cm^{-1}, while their vibrational frequency ranges are 46.90–210.92, 39.17–234.72, and 37.12–217.94 cm^{-1}, indicating a narrow range for their vibrational spectra. For comparison, we have evaluated the bare Ag_{19} cluster, which shows the main vibrational mode at 75.82 cm^{-1}, within a range of 22.11–225.92 cm^{-1}.

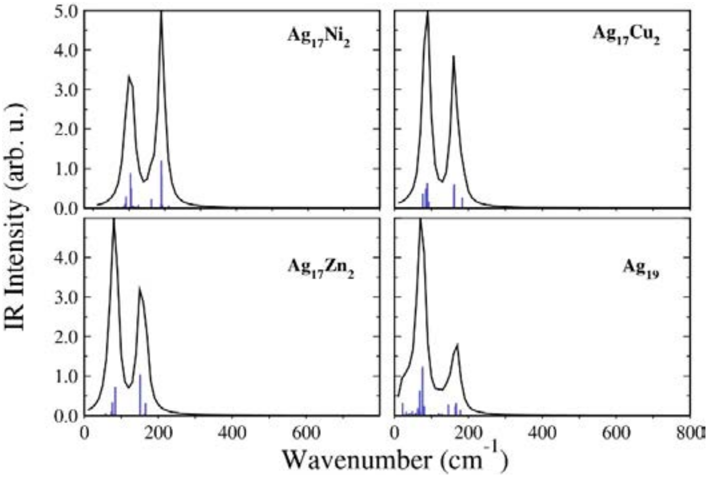

Figure 2: IR Spectra for $Ag_{17}M_2$ (M = Ni, Cu, Zn) Clusters Obtained at the PBE0/Def2-ECP Level. The Bare Ag_{19} Clusters is Shown for Comparison.

To investigate the stability and reactivity of double icosahedron $Ag_{17}M_2$ (M = Ni, Cu, Zn) clusters, we summarized the calculated parameters in Table I. The results show that doping the Ag_{19} cluster increases the ionization energy, while the electron affinity does not show a specific trend upon doping. The derived parameters such as the chemical hardness (η) and electronegativity (χ) show increased values for the doped clusters compared to the bare Ag_{19} cluster, suggesting that the doped clusters are more prone to accepting electrons. These findings provide valuable insights into the tunability of Ag-based nanoclusters for potential applications in catalysis and electronic materials.

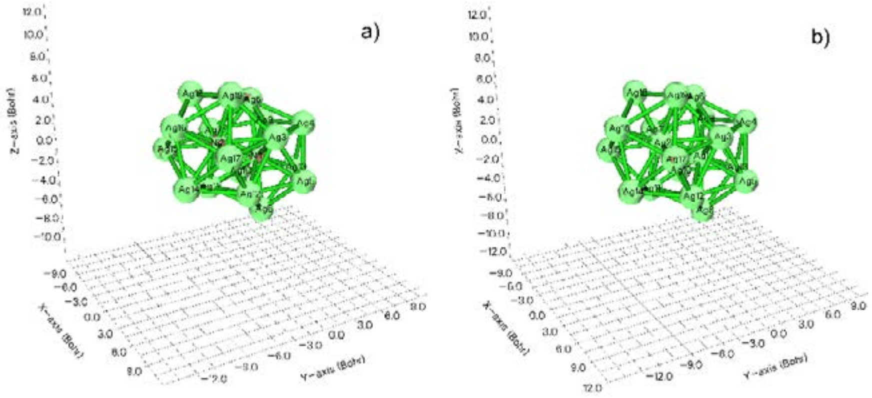

Figure 3: The Electron Localization Function (ELF = 0.7) for a) the $Ag_{17}Ni_2$ Cluster and b) the Ag_{19} Cluster.

Cluster	I	A	η	χ	ω
$Ag_{17}Ni_2$	5.67	2.40	1.63	4.04	5.00
$Ag_{17}Cu_2$	5.45	2.48	1.48	3.96	5.29
$Ag_{17}Zn_2$	5.76	2.55	1.60	4.15	5.39
Ag_{19}	5.36	2.45	1.45	3.91	5.26

Table 2: The Ionization Energy (I), Electron Affinity (A), Chemical Hardness (η), Electronegativity (χ) and Electrophilicity Index (ω) of $Ag_{17}M_2$ (M = Ni, Cu, Zn) and Ag_{19} Clusters. The Results are Calculated With the PB86 Functional in Conjunction With the Def2-ECP Basis set. The Energy is Given in eV.

To gain insight into the reactivity of the clusters, we evaluated the ELF distribution, which indicates where electrons are localized and helps identify active sites that are either electron-rich (nucleophilic) or electron-deficient (electrophilic). These sites may correspond to bonding interactions between atoms or molecules with the cluster. In a metal nanoparticle catalyst, it is well established that atoms at edges and corners exhibit higher reactivity due to their lower coordination numbers [22, 23]. This increased reactivity is associated with enhanced electron localization, which facilitates interactions with reactants. We expect high ELF values to indicate regions where electrons are highly localized and likely to interact with reactants. As shown in Figure 3, the doped clusters, for example, $Ag_{17}Ni_2$, exhibit more localized sites on the Ag surfaces but greater depletion at the central sites, which can be contrasted with the bare

Ag19 cluster. These preliminary results provide a foundation for further exploration of cluster reactivity, with potential applications in catalysis [24–29].

3. Conclusions

In this work, the structural and electronic properties of $Ag_{17}M_2$ (M = Ni, Cu, Zn) clusters are investigated using density functional theory (DFT) calculations. The DFT analysis of the clusters confirms their preference for endohedral configurations in the doublet state across multiple functionals. Doping enhances the ionization energy and electronegativity of the clusters compared to the bare Ag_{19} counterpart, indicating increased stability. Furthermore, the observed increase in ELF values at Ag sites suggests enhanced electron localization, which may have significant implications for catalysis.

Acknowledgments

P.L.R.-K. would like to thank the support of CIMAT Supercomputing Laboratories of Guanajuato and Puerto Interior.

Reference

1. Baletto, F. (2019). Structural properties of sub-nanometer metallic clusters. Journal of Physics: Condensed Matter, 31(11), 113001.
2. Jiang, Y. Q., Peng, P., Wen, D. D., Han, S. C., & Hou, Z. Y. (2015). A DFT study on the heredity-induced coalescence of icosahedral basic clusters in the rapid solidification. Computational Materials Science, 99, 156-163.
3. Yeh, C. H., Lin, Y. C., & Ho, J. J. (2014). Highly effective catalysis of the double-icosahedral Ru 19 cluster for dinitrogen dissociation–a first-principles investigation. Physical Chemistry Chemical Physics, 16(16), 7394-7400.
4. Yamamoto, K., Imaoka, T., Chun, W. J., Enoki, O., Katoh, H., Takenaga, M., & Sonoi, A. (2009). Size-specific catalytic activity of platinum clusters enhances oxygen reduction reactions. Nature chemistry, 1(5), 397-402.
5. Qaseem, A., Chen, F., Wu, X., & Johnston, R. L. (2016). Pt-free silver nanoalloy electrocatalysts for oxygen reduction reaction in alkaline media. Catalysis Science & Technology, 6(10), 3317-3340.
6. Corona, B., Howard, M., Zhang, L., & Henkelman, G. (2016). Computational screening of core@ shell nanoparticles for the hydrogen evolution and oxygen reduction reactions. The Journal of Chemical Physics, 145(24).
7. Rodríguez-Carrera, S., Rodríguez-Kessler, P. L., Ambriz-Vargas, F., Garza-Hernández, R., Reséndiz-Ramírez, R., Martínez-Flores, J. S., ... & Muñoz-Castro, A. (2024). First principles study for Ag-based core-shell nanoclusters with 3d-5d transition metal cores for the oxygen reduction reaction. Inorganica Chimica Acta, 572, 122301.
8. Yang, S., Rao, D., Ye, J., Yang, S., Zhang, C., Gao, C., ... & Yan, X. (2021). Mechanism of transition metal cluster catalysts for hydrogen evolution reaction. International Journal of Hydrogen Energy, 46(5), 3484-3492.
9. Neese, F., Wennmohs, F., Becker, U., & Riplinger, C. (2020). The ORCA quantum chemistry program package. The Journal of chemical physics, 152(22).
10. Weigend, F., & Ahlrichs, R. (2005). Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Physical Chemistry Chemical Physics, 7(18), 3297-3305.
11. Weigend, F. (2006). Accurate Coulomb-fitting basis sets for H to Rn. Physical chemistry chemical physics, 8(9), 1057-1065.
12. Andrae, D., Häußermann, U., Dolg, M., Stoll, H., & Preuss, H. (1990). Energy-adjusted ab initio pseudopotentials for the second and third row transition elements. Theoretica chimica acta, 77, 123-141.
13. Dolg, M., Wedig, U., Stoll, H., & Preuss, H. (1987). Ab initio pseudopotential study of the first row transition metal monoxides and iron monohydride. The Journal of chemical physics, 86(4), 2123-2131.
14. Lu, T., & Chen, F. (2012). Multiwfn: A multifunctional wavefunction analyzer. Journal of computational chemistry, 33(5), 580-592.
15. Koopmans, T. (1934). Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den einzelnen Elektronen eines Atoms. physica, 1(1-6), 104-113.
16. Pearson, R. G. (2005). Chemical hardness and density functional theory. Journal of Chemical Sciences, 117, 369-377.
17. Rodríguez-Kessler, P. L., & Muñoz-Castro, A. (2023). Structure and stability of Mo-doped Cun (n= 1–12) clusters: DFT calculations. Inorganica Chimica Acta, 556, 121620.
18. Rodríguez-Kessler, P. L., Vásquez-Espinal, A., & Muñoz-Castro, A. (2023). Structure and stability of Cu-doped Bn (n= 1–12) clusters: DFT calculations. Polyhedron, 243, 116538.
19. Rodríguez-Kessler, P. L., Rodríguez-Carrera, S., & Muñoz-Castro, A. (2024). Hydrogen evolution reaction on Ag12M icosahedrons: A DFT study. Chemical Physics Letters, 856, 141588.
20. Rodríguez-Kessler, P. L. (2024). On the structures and stabilities of B $ _7 $ Cr $ _2 $ clusters: A DFT study. arXiv preprint arXiv:2407.20498.
21. Rodríguez-Kessler, P. L. (2024). Revisiting the Global Minimum Structure of the Pt5V Cluster. arXiv preprint arXiv:2408.03537.
22. Zhang, C., Shen, X., Pan, Y., & Peng, Z. (2017). A review of Pt-based electrocatalysts for oxygen reduction reaction. Frontiers in Energy, 11, 268-285.
23. Shao, M., Peles, A., & Shoemaker, K. (2011). Electrocatalysis on platinum nanoparticles: particle size effect on oxygen reduction reaction activity. Nano letters, 11(9), 3714-3719.
24. Rodríguez-Kessler, P. L., & Rodríguez-Domínguez, A. R. (2015). Size and structure effects of PtN (N= 12–13) clusters for the oxygen reduction reaction: First-principles calculations. The Journal of Chemical Physics, 143(18).
25. Rodríguez-Kessler, P. L., Muñoz-Castro, A., Rodríguez-Domínguez, A. R., & Cabellos, J. L. (2023). Structure effects of Pt 15 clusters for the oxygen reduction reaction: first-

Citation: Rodríguez-Kessler, P. L. (2025). Stability and Reactivity of Double Icosahedron Ag17M2 (M=Ni, Cu, Zn) Clusters. *J Theor Phys Math, 3* (1), 1-5.

principles calculations. Physical Chemistry Chemical Physics, 25(6), 4764-4772.

26. Li, W., Feng, H., & Shang, R. (2024). First Principle Study on Structural, Electronic, Magnetic, and Optical Properties of Co-Doped Middle Size Silver Clusters. Molecules, 29(11), 2670.
27. Wei, P., Zheng, J., Li, Q., Qin, Y., & Song, L. (2022). The role of silver in 13-atom palladium-silver bimetallic clusters: nucleation and growth, structural evolution, electron interaction. Journal of Materials Science, 57(17), 8180-8194.
28. Hu, J., Ma, J., Jin, Z., Liu, W., Huang, L., Wang, X., & Xing, X. (2024). Reactivity of cationic silver clusters with O 2: a probe of interplay between clusters' geometric and electronic structures. Physical Chemistry Chemical Physics, 26(9), 7407-7415.
29. Jalili, S., Goliaei, E. M., & Schofield, J. (2017). Silver cluster supported on nitrogen-doped graphene as an electrocatalyst with high activity and stability for oxygen reduction reaction. international journal of hydrogen energy, 42(21), 14522-14533.

Citation: Rodríguez-Kessler, P. L. (2025). Stability and Reactivity of Double Icosahedron Ag17M2 (M=Ni, Cu, Zn) Clusters. *J Theor Phys Math, 3* (1), 1-5.