

## $\sigma$ Aromaticity of the Bimetallic $\text{Au}_5\text{Zn}^+$ Cluster

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Aromaticity is a conventional and useful concept for understanding the enhanced stability of conjugated  $\pi$ -bonding systems in organic compounds such as benzene ( $\text{C}_6\text{H}_6$ ) and the cyclopentadienyl anion ( $\text{C}_5\text{H}_5^-$ ). Although the definition and physical origin of aromaticity are still being argued,<sup>1,2</sup> a planar and cyclic geometry as well as ring currents provided by delocalization of  $(4n + 2)$   $\pi$  electrons are widely accepted as criteria for aromaticity. Schleyer et al. discussed the definition of aromaticity and concluded that aromaticity could be uniquely defined by magnetic criteria such as diamagnetic susceptibility exaltation.<sup>3,4</sup> The calculation of nucleus-independent chemical shifts (NICSS) has been proposed as an efficient aromaticity probe.<sup>5</sup> Recently, the applicability of the aromaticity concept has been expanded to metallic clusters in a combined photoelectron spectroscopy and *ab initio* molecular orbital (MO) calculational investigation of  $\text{M}_4^{2-}$  (Al, Ga, and In) clusters.<sup>6</sup> The square  $\text{M}_4^{2-}$  has two delocalized  $\pi$  electrons, satisfying the  $(4n + 2)$  electron counting rule. Not only a  $\pi$ -bonded highest occupied MO (HOMO) accommodating the two electrons but also two  $\sigma$ -bonded MOs below the HOMO contribute to the stability and planarity of the species, providing  $\pi$  and  $\sigma$  aromaticity for the system. For  $\text{Al}_4^{2-}$ , Fowler et al. reported that unconventional diamagnetic ring currents originate in the  $\sigma$  system and have negligible contribution from the  $\pi$  system.<sup>7</sup> These concepts were recently extended to other metallic species.<sup>8</sup>

In this communication, we present the first example of an aromatic bimetallic cluster involving only  $\sigma$  orbitals. Our photo-fragmentation experiments have revealed that  $\text{Au}_5\text{X}^+$  ( $\text{X} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$ ) clusters show an anomalously high stability in mass abundance spectra of  $\text{Au}_N\text{X}^+$  clusters.<sup>9</sup> Here, we present even more compelling experimental evidence for an enhanced stability of the  $\text{Au}_5\text{Zn}^+$  cluster. Theoretical calculations suggest that this planar cluster with six valence electrons provides a strong magnetic shielding inside and above the structure caused by a diamagnetic ring current effect. The enhanced stability of  $\text{Au}_5\text{Zn}^+$  may be ascribed to its aromaticity.

The  $\text{Au}_N\text{Zn}^+$  clusters were produced in a dual-target dual-laser vaporization source<sup>10</sup> and were investigated with cationic photo-fragmentation mass spectrometry. In this experiment, information is obtained on the relative stability of cluster cations as a function of their size, as a result of ionization and fragmentation following multiphoton absorption. Fragments with an enhanced stability will be more prominent. Figure 1 shows the measured mass abundance of  $\text{Au}_N\text{Zn}^+$  ( $N = 2-44$ ) clusters. The abundance of  $\text{Au}_5\text{Zn}^+$  stands out, implying a high stability of this species. An electronic shell model interpretation,<sup>11,12</sup> which successfully explains stability patterns observed in mass abundance spectra of  $\text{Au}_N\text{X}^+$  clusters,<sup>9</sup> suggests that  $\text{Au}_5\text{Zn}^+$  has six delocalized electrons.

We carried out *ab initio* calculations to optimize geometries of  $\text{Au}_5\text{Zn}^+$  and examined their electronic structures and magnetic properties.<sup>13</sup> A relativistic effective core potential and the corresponding valence basis sets were adopted for Au atoms. The

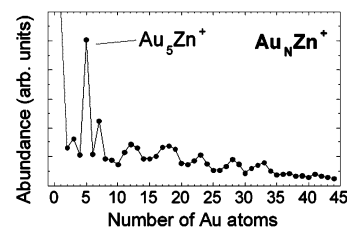


Figure 1. Mass abundance of  $\text{Au}_N\text{Zn}^+$  clusters measured with cationic photo-fragmentation mass spectrometry.

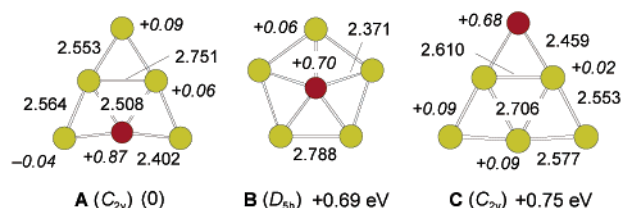
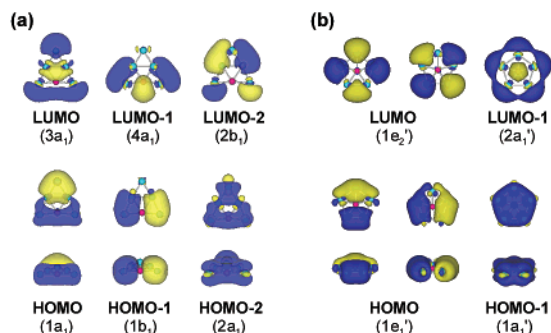


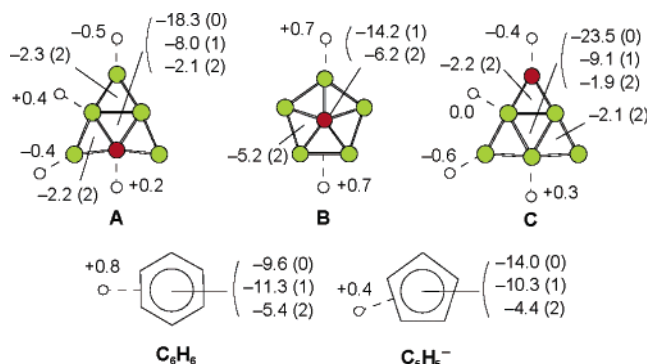
Figure 2. Optimized structures, charge populations, and relative stability of  $\text{Au}_5\text{Zn}^+$  calculated at the MP2 level of theory. Bond distances are presented in Å. Charge populations are given in italics.

importance of including relativistic effects was elucidated by recent calculations.<sup>18,19</sup> Figure 2 shows three structural isomers of the  $\text{Au}_5\text{Zn}^+$  cluster. No three-dimensional structures were found in the present study. The lowest-energy isomer A has a triangular structure in which the Zn atom locates on a side of the triangle. The high symmetric pentagonal isomer B is 0.69 eV less stable than isomer A, because insertion of the Zn atom into a  $\text{Au}_5$  pentagon elongates the Au–Au bond distances. The triangular isomer C, in which the Zn atom is located at an apex of the triangle, is 0.75 eV less stable than isomer A. Because the Au–Zn bond energy<sup>20</sup> (3.67 eV) is larger than the Au–Au bond energy<sup>21</sup> ( $2.290 \pm 0.008$  eV), isomer A, which has four Au atoms adjacent to the Zn atom, is more stable than isomer C, which has only two Au–Zn bonds. Aromatic organic compounds generally have a high symmetrical structure such as  $D_{6h}$  for  $\text{C}_6\text{H}_6$  and  $D_{5h}$  for  $\text{C}_5\text{H}_5^-$ . In the case of  $\text{Au}_5\text{Zn}^+$ , isomer B with  $D_{5h}$  symmetry is less stable than isomer A with  $C_{2v}$  symmetry. Schleyer et al. pointed out that structural criteria such as bond length equalization could not be used to characterize aromaticity uniquely.<sup>3,4</sup> On the basis of these arguments, one may consider cyclic delocalization of valence electrons to be more important than the symmetry of the molecular frame to characterize aromaticity.

To examine the electron delocalization of  $\text{Au}_5\text{Zn}^+$ , the spatial distribution of the HOMOs is depicted in Figure 3. Six valence s electrons occupying these MOs delocalize over the entire structure, so that these electrons contribute to both the Au–Au and the Au–Zn bonds. As shown in Figure 2, charge population analysis showed that the Au atoms are nearly neutral while the Zn atom loses one 4s electron to make the cluster cationic. Six s electrons do not localize at a specific site in the structure. The electron delocalization may play a significant role in stabilizing the structure of  $\text{Au}_5\text{Zn}^+$ .



**Figure 3.** HOMOs and LUMOs of the isomers A (a) and B (b). For the LUMO levels, only the top view images of the MOs are given; for the HOMO levels also side views (tilted by 10°) are shown to clarify nodal properties.



**Figure 4.** Nucleus-independent chemical shifts (NICSs) in ppm for the isomers of Au<sub>5</sub>Zn<sup>+</sup> and aromatic organic compounds (C<sub>6</sub>H<sub>6</sub> and C<sub>5</sub>H<sub>5</sub><sup>-</sup>) calculated with the GIAO-HF method. The values in parentheses represent the distances in Å from the molecular plane.

The MO pattern of Au<sub>5</sub>Zn<sup>+</sup> depicted in Figure 3 resembles those of aromatic organic compounds such as C<sub>6</sub>H<sub>6</sub> and C<sub>5</sub>H<sub>5</sub><sup>-</sup>, except for their nodal properties in the molecular plane. The Au<sub>5</sub>Zn<sup>+</sup> cluster only has  $\sigma$ -bonded MOs in its HOMO level unlike the Al<sub>4</sub><sup>2-</sup> cluster where one  $\pi$  MO and two  $\sigma$  MOs contribute to the stability.<sup>6</sup>

Finally, we performed NICS calculations to predict magnetic properties of Au<sub>5</sub>Zn<sup>+</sup>.<sup>22</sup> NICS calculations,<sup>5</sup> which allow one to quantify the strength of the magnetic shielding, have been applied to characterize the aromaticity of various organic and inorganic compounds,<sup>5,23</sup> planar borocarbons,<sup>24</sup> and three-dimensional inorganic compounds.<sup>25</sup> A large negative NICS at the ring center (or inside and above a molecular frame) implies the presence of diamagnetic ring currents, because ring currents induced by an external magnetic field generate a shielding magnetic field. A deshielding effect by the ring current should provide a positive NICS value outside of the molecular frame. Here, we calculated NICS values not only inside or above ( $\delta_{in}$ ) but also outside ( $\delta_{out}$ ) of the molecular frame. The values of  $\delta_{in}$  were obtained at several points inside the molecular frame [ $\delta_{in}(0)$ ] and 1 or 2 Å above the point where  $\delta_{in}(0)$  was calculated [ $\delta_{in}(1)$  or  $\delta_{in}(2)$ ]. The value of  $\delta_{out}$  was obtained at points 2 Å outside of the molecular frame, in the molecular plane. Figure 4 shows the result of NICS calculations for Au<sub>5</sub>Zn<sup>+</sup> together with those for C<sub>6</sub>H<sub>6</sub> and C<sub>5</sub>H<sub>5</sub><sup>-</sup>. NICS values for these organic compounds are large and negative inside and above the carbon ring and positive outside of the ring, implying that delocalized electrons in both compounds provide diamagnetic ring currents. For Au<sub>5</sub>Zn<sup>+</sup>, all of the isomers give a large negative  $\delta_{in}(0)$  comparable to the aromatic organic compounds. Especially for isomer B, large values of  $\delta_{in}(2)$  (-6.2 and -5.2) and  $\delta_{out}$  (+0.7) are found. The sign and amplitude of  $\delta_{out}$  for isomers A and C depend on the position where the calculation is carried out, probably

due to the low geometric symmetry. The NICS values obtained here prove that the diamagnetic ring current effect, characteristic for aromaticity, exists in the Au<sub>5</sub>Zn<sup>+</sup> cluster. It is notable that Au<sub>5</sub>Zn<sup>+</sup> with six  $\sigma$  electrons satisfies the criterion for aromaticity despite having no occupied  $\pi$  MOs. From all of the results of our calculation on electronic structures and magnetic properties, we conclude that the Au<sub>5</sub>Zn<sup>+</sup> cluster can be regarded as a  $\sigma$  aromatic bimetallic cluster with six delocalized s electrons.

**Acknowledgment.** We thank P. v. R. Schleyer for valuable discussions. This work is financially supported by the Fund for Scientific Research – Flanders (Belgium) (FWO), by the Flemish Concerted Action (GOA) Research Program, and by the Belgian Interuniversity Poles of Attraction Program (IAP). S.N. and E.J. are Research Assistants of the FWO.

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JA029157C