The Peculiar Role of the Au$_3$ Unit in Au$_m$ Clusters: $\sigma$-Aromaticity of the Au$_5$Zn$^+$ Ion

Yanle Li, Vytor Oliveira, Chunmei Tang, Dieter Cremer, Chunyan Liu, and Jing Ma

1. INTRODUCTION

Gold clusters have received enhanced interest in nanoscience because of their unique catalytic, electronic, and optical properties. The pronounced scalar relativistic effects of gold lead to the fact that Au$_m$ clusters exhibit unique structural and bonding properties that distinguish them from other metal clusters.1 During the past three decades, pure gold clusters Au$_m$ in the small-to-medium size range have been described in experimental and theoretical studies. In 2008, Gruene and co-workers determined the structure of neutral Au$_7$, Au$_{19}$, and Au$_{20}$ by comparing their experimental spectra obtained by far-IR multiple-photon dissociation (FIR-MPD) spectroscopy in the gas phase with the calculated vibrational spectra for multiple isomers.7 De and co-workers investigated the finite temperature behavior of neutral Au$_m$ (m = 3–10) clusters in the gas phase using molecular dynamical simulations based on relativistic density functional theory (DFT).8 Zanti and Peeters studied Au$_m$ (m ≤ 16) clusters with B3LYP and explained their stability in terms of a donor–acceptor model, which suggested a cyclic flow of electrons within a cluster.9 Sergeeva and Boldyrev demonstrated that small three-dimensional Au clusters could be built from the Au$_4$ tetrahedron characterized by 4c-2e bonding.10 All these investigations established a deeper insight into the structure and thermodynamic stability of gold clusters. Recently, Xu and co-workers used the triangular, two-electron (2e) Au$_3$ (in short: Au$_3$(2e)) and rhombic Au$_5$(2e) rings as elementary units to investigate the stabilities of 71 reported thiolate-protected Au nanoclusters developing and applying the Grand Unified Model (GUM).11 On the basis of GUM, the authors not only rationalized the stabilities of known thiolate-protected gold nanoclusters but also predicted new ligand-protected gold nanoclusters of distinct stability. Gilb and co-workers studied small Au cluster cations (Au$_m^+$, m < 14) utilizing ion mobility measurements and computational methods and found that gold cluster cations had planar structures for m = 3–7 at room temperature.12

The concept of $\sigma$-aromaticity (stabilization by 4p + 2 $\sigma$-electrons in radial or 4p $\sigma$-electrons in tangential occupied orbitals, p = 0, 1, 2, ..., thus leading to aromatic Hückel and/or aromatic Möbius systems) can be traced to two different delocalization modes:13,14 (i) Peripheral (one-dimensional) delocalization along the $\sigma$-bonds: In 1979, Dewar15 discussed the small ring strain of cyclopropane and related this to the peripheral delocalization of $\sigma$-electrons. (ii) Surface (two-dimensional) delocalization in the ring plane: Cremer and Kraka13,14 showed that $\sigma$-delocalization could lead to delocalization in the ring plane of cyclopropane, which in substituted cyclopropanes demonstrated both geometry and stability. Later, Cremer and Gauss16 provided further evidence for the phenomenon of surface delocalization. The potential $\sigma$-aromaticity of various small rings has caught the interest of many researchers.17–19 The physical and chemical properties of hydrogen clusters,20 polycyclophosphasenes,21 Zn$_3^+$ and Ge$_4^{2+}$ clusters,22,23 lanthanum-doped boron clusters,24 and unsaturated cyclopropametallapentalenes25,26 have also been rationalized in terms of $\sigma$-aromaticity or surface delocalization.
To our knowledge, a systematic theoretical investigation of the stabilities of planar \( \text{Au}_m \) clusters as an aggregation of \( \text{Au}_3(2e) \) or \( \text{Au}_3(3e) \) building blocks has not been performed so far. As becomes obvious from Scheme 1, the ground states of \( \text{Au}_m \) clusters contain \( \text{Au}_3 \) units (\( \text{Au}_3 \) rings with \( 2 \leq p \leq 3 \) electrons), suggesting a simple structural principle for gold clusters. In this work, we will present an electronic structure description of the \( \text{Au}_3 \) units based on their energetic, geometric, vibrational, magnetic, and electron density properties and use the outcome of this analysis to discuss structure and stabilities of planar \( \text{Au}_m \) clusters up to \( m = 7 \) for the purpose of obtaining a general building principle for \( \text{Au}_m \) clusters. Apart from this, \( \text{Au}_5 \text{Zn}^+ \) will be analyzed, as it is an electronically interesting analogue of the \( \text{Au}_6 \) cluster and also a potential \( \sigma \)-aromatic cluster.27

### 2. COMPUTATIONAL DETAILS

Geometry optimizations and vibrational frequency calculations were performed for all \( \text{Au}_m \) clusters shown in Scheme 1 utilizing DFT. Becke’s three-parameter hybrid exchange-correlation functional (B3LYP)28,29 was used in connection with the LANL2DZ basis set30−32 (for Zn, the 6-31G(d) basis set was employed). Preliminary calculations were also performed with the CAM-B3LYP,33 M06,34 M06-2X,34 LC-oPBE,35−37 and \( \omega \)B97XD38 functionals. It turned out that B3LYP was more robust for the calculation of second-order response properties, and therefore most of the results were discussed for this hybrid functional. Each stationary point was verified to be a minimum on the potential energy surface with the help of the eigenvalues of the Hessian matrix of second derivatives. At the B3LYP/LANL2DZ level, the \( T_d \)-symmetrical \( \text{Au}_4 \) and the \( D_{6h} \)-symmetrical \( \text{Au}_6 \) clusters were located as stationary points with three and one imaginary frequencies, respectively, which was the reason why these two structures were not investigated in detail, although their relative stability was discussed in this work.

CCSD(T)39 and PBEPBE-D3(BJ)40−42 calculations with an aug-cc-pVTZ-PP basis set34,44 were also performed to predict the atomization
Scheme 2. Overview of the Methods Used in This Work^2^

\[ n = a(k^b) \]  

where the constants \( a \) and \( b \) are determined via the two reference molecules and the requirement that for \( k = 0 \) the BSO value must be also zero. Analysis of the relativistically corrected electron density obtained with the Dirac-exact Normalized Elimination of the Small Component (NESC) method^57,58 reveals that the MO-based assumption of bond orders given above underestimates bonding for \( \text{Au}_3^{+} \). The more reliable Mayer bond orders^59,60 suggest \( n \)-values of 1.105 and 0.610 for \( \text{Au}_2 \) and \( \text{Au}_3^{+} \), respectively (for B3LYP/LANL2DZ, \( k \)' values of 1.567 and 0.833 mdyr/\AA \(^2\) were obtained), which lead to a power relationship (1) with \( a = 0.724 \) and \( b = 0.941 \). All BSO values were calculated using eq 1 based on these constants.

Sometimes it is useful to scale BSO values so that the total number of valence electrons is reproduced. Although the scaled BSO values are no longer comparable with those of other molecules with different atoms, they provide an impression on the number of electrons in a 3-ring.

The charge distribution in the \( \text{Au}_m \) clusters was determined using the natural population analysis (NPA) by Weinhold and co-workers. This approach was also employed to determine natural bond orders (NBOs) and to probe the possible existence of non-Lewis bonds with 3c-character. The electron density analysis of Bader^62 was applied to find bond critical points (BCPs) and ring critical points (RCPs) of the electron density distribution \( \rho(z) \). The Laplacian of \( \rho(z) \) in the z-direction (normal to the ring plane), \( \nabla^2 \rho(z) \), was used to investigate any density concentration in the center of the 3-ring. Larger density concentration is indicated by a more negative \( \nabla^2 \rho(z) \) value.

Cremer and co-workers have derived an aromaticity index (AI) from local stretching force constants and their associated BSO values. In this work, we extend the definition of AI to describe \( \sigma \)-delocalization and the nonclassical bonding character in \( \text{Au}_m \) clusters: For this purpose we use eq 2

\[ \text{AI} = 1 - \frac{\gamma}{N_{\text{bonds}}} \sum (n_{\text{opt}} - n_{\text{i}})^2 \]  

where \( n_{\text{opt}} = 0.610 \) gives the optimal BSO of \( \text{Au}_3^{+} \) at the B3LYP/LANL2DZ level of theory, \( n_{i} \) the BSO value of the \( i \)-th bond, \( N_{\text{bonds}} \) is the number of bonds in an \( \text{Au}_m \) ring, and \( \gamma = 4.078 \) is an adjustable parameter that sets the AI of the reference molecule \( \text{Au}_3^{+} \) equal to 1 (or 100%) thus identifying a completely delocalized 3c-2e system. Any

energies (AE) and normalized AE (NAE or cohesive energy) of the planar clusters: NAE = AE/\( N \), where \( N \) is the number of atoms in a molecule. In the case of the \( \text{Au}_3(3e) \) multireference system, CASSCF and broken-symmetry unrestricted DFT (BS-UDFT) calculations were performed to estimate its stability. 

For the description of delocalization and potential aromaticity, we calculated the nucleus-independent chemical shift (NICS) parameters utilizing the Gauge-Independent Atomic Orbital (GIAO) method. The NICS value gives the negative of the magnetic shielding computed at a prechosen position of the molecular geometry. In this work, NICS values are calculated at the centroids of the rings (denoted as NICS(0)) and 1.0 Å above the ring centroids (NICS(1)) to exclude to some extend the in

\( \sigma \)-aromaticity of \( \text{Au}_m \)

\begin{align*}
\text{Energy-based Properties} \\
\text{Atomization energy (AE)} \\
\text{Normalized AE (NAE)} \\
\text{Vibrational Properties} \\
\text{(IR / Raman based)} \\
\text{Bond strength order (BSO)} \\
\text{Electronic Density Properties} \\
\text{Electron localization function (ELF)-\( \sigma \)} \\
\text{Aromaticity index (AI)}
\end{align*}

\[ \text{Magnetic Properties} \]

\[ \text{Nucleus-independent chemical shift (NICS)} \]

\[ \text{NICS(1) -14 ppm} \]

\[ \text{NICS(0) -31 ppm} \]

\[ \text{The NICS(0) and NICS(1) values (in ppm) of \( \text{Au}_3^{+} \) are taken at pre-chosen positions indicated by the red dots: for NICS(0), the geometrical center (centroid) of the ring is taken, for NICS(1) the position 1 Å above the centroid of the \( \text{Au}_3^{+} \) ring.} \]
Al value smaller than 1 indicates a less delocalized σ-electron system. For AI = 0, classical covalent 2e-2e bonding is fully established as it is found in Au2.

Parameters such as AI can be used to determine σ-aromaticity ( peripheral delocalization in a Au6 ring), whereas \( V^2 \rho(z) \) measures the concentration of the energy density at the RCP, which reflects the degree of surface delocalization and is especially important in organic 3-rings and π-complexes.\(^1\) One can weight \( \rho(RCP) \) with \( V^2 \rho(z) \) to get \( \eta = \rho(RCP)/V^2 \rho(z) \), an area reflecting the extent of surface delocalization. If the concentration is large, the area becomes small; that is, less delocalization; that is, concentration and delocalization of electrons are opposing properties. AI, \( V^2 \rho(z) \), and \( \eta \) reflect the degree of electron delocalization, but they do not reflect other electronic factors such as ring strain or \( \pi \)-complex character of a 3-ring.\(^1\) Therefore, the deviation \( d \), of the maximum electron density path ( bond path) from the internuclear connection line at the BCP was calculated. Also, the extent of ring strain was evaluated by determining the deformation coordinates\(^66\) \( R \) (breathing radius \( R \) of 3-ring; \( R = R_0 \) = \( t_0 \) is the deviation from a suitable reference radius \( R_0 \)), \( t_1 \) (deformation amplitude), and \( \phi_1 \) (deformation phase angle). Once the deformation coordinates are known, the associated local deformation force constants\(^66\) can be calculated that provide a direct measure of ring strain. Calculations were performed with Gaussian09,\(^67\) Molpro,\(^68\) and the COLOGNE2016 program.\(^69\) ELF calculations were performed with the Multifun package.\(^60\)

3. RESULTS AND DISCUSSIONS

The optimized planar structures of Au\(_{3+}^+\), Au\(_{m}\) (\( m = 4\)−7), and cation Au\(_{m}\)Zn\(^+\) are displayed in Scheme 1 (for the Cartesian coordinates of the equilibrium geometries, see the Supporting Information). All structures calculated are planar or nearly planar. Their relative stabilities are determined via the corresponding AE and NAE values (Table 1 and Figure S1).

Table 1 and Figure S1 reveal that Au\(_{3+}^+\) represents (compared with Au\(_{m}\) Au\(_{m}\)Zn\(^+\), and Au\(_{m}\)Zn\(^+\)) a stable Au\(_{m}\) cluster (NAE, PBEPBE-D3(BJ)): 47.3 kcal/mol; CCSD(T): 42.5 kcal/mol, comparable in its stability with Au\(_{6}\) (46.1; 43.1 kcal/mol) and Au\(_{7}\) (45.3 kcal/mol, Table 1). Noteworthy is that all Au clusters investigated have a larger NAE than Au\(_{6}\) (27.3; 24.7 kcal/mol), which suggests that planar Au\(_{m}\) rings gain a significant amount of stabilization, which obviously has to do with electron delocalization in the 3-ring units.

The energy differences between the frontier orbitals of Au\(_{m}\)\(^+,\) Au\(_{m}\) and Au\(_{m}\)Zn\(^+\) calculated with different exchange-correlation (XC) functionals are shown in Figure 1 and Table S1. Although the magnitude of the highest occupied molecular orbital—lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps, \( \Delta \epsilon \), changes with the XC functional used, all XC functionals (with the exception of PBEPBE) predict the same order of \( \Delta \epsilon \) values: Au\(_{3+}^+\) > Au\(_{m}\)Zn\(^+\) > Au\(_{m}\) > Au\(_{6}\) > Au\(_{5}\) > Au\(_{4}\). This trend does not exactly follow the trend of the calculated NAE in Table 1, but there are some similarities.

In addition to the energy gaps, the results of the NICS and ELF-σ calculations are shown in Figure 1 and Table S1. The difference in the NICS(0) and NICS(1) values indicates that the \( \sigma \) frame has significant influence on NICS(0), which makes it advisable to base the analysis of the magnetic properties of the Au clusters investigated exclusively on NICS(1).

The NBO analysis of Au\(_{3+}^+\) confirms that the 6s orbitals of the Au atoms form an \( a_1^-\)-symmetrical, bonding 3c-orbital, that is, a fully delocalized orbital. Hence, it is justified to speak of a \( \sigma\)-aromatic 2e-ensemble that determines the stability and geometry of Au\(_{3+}^+\). The scalar relativistic contraction of the 6s(Au) orbital and the positive charge both lead to a decrease of the energy of the 3c orbital, a shortening of the Au–Au

<table>
<thead>
<tr>
<th>Table 1. Calculated Atomization Energies (AE) and Normalized Atomization Energies (NAE)(^a)</th>
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<tr>
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<tr>
<td>Au(<em>{1})(D$</em>{2h}$) → 2Au (( 2S ))</td>
</tr>
<tr>
<td>Au(<em>{1})(2e) (D$</em>{2h}$) → 2Au (( 2S )) + 1Au (( 1S ))</td>
</tr>
<tr>
<td>Au(<em>{1})(3e) (C$</em>{3v}$) → 3Au (( 2S ))</td>
</tr>
<tr>
<td>Au(<em>{1})(3e) (C$</em>{2v}$) → 3Au (( 2S ))</td>
</tr>
<tr>
<td>Au(<em>{1})(D$</em>{3h}$) → 4Au (( 2S ))</td>
</tr>
<tr>
<td>Au(<em>{1})(C$</em>{m}$) → 4Au (( 2S ))</td>
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<td>Au(<em>{1})(C$</em>{m}$) → 5Au (( 2S ))</td>
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<td>Au(<em>{1})(C$</em>{m}$) → 6Au (( 2S ))</td>
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<td>Au(<em>{1})(C$</em>{m}$) → 7Au (( 2S ))</td>
</tr>
<tr>
<td>Au(<em>{1})(C$</em>{m}$) → 2Au (( 2S )) + Zn (( 2S ))</td>
</tr>
<tr>
<td>Au(<em>{1})(C$</em>{m}$) → 2Au (( 2S )) + Zn (( 2S ))</td>
</tr>
</tbody>
</table>

\(^a\) In kilocalories per mole. \(^b\) CCSD(T) energies at PBEPBE-D3(BJ)/aug-cc-pVTZ-PP geometries. \(^c\) Broken symmetry solutions. UPBEPBE leads to an imaginary frequency of 210 i cm$^{-1}$. |
bonds, thereby an increase of the Au–Au bond strength, and an overall stabilization of the cation. Kalesky and co-workers\(^1\) have coined in this connection the term electronegativity-driven increase of bond strength, which applies in the case of Au\(^+\) as the effective electronegativity of Au increases with regard to the 6s electrons. Scalar relativity also leads to an expansion of the 5d lone pair orbitals and to an increase of their energies, which leads to overall destabilizing contributions. The strong decrease of the \(\Delta\varepsilon\) HOMO relative to the e\(^-\) LUMOs causes the increase in \(\Delta\varepsilon\) (Figure 1, Table S1). This observation causes two questions, which must be answered in the following: (i) Is \(\sigma\)-electron delocalization a typical phenomenon for Au clusters? (ii) The 3e system Au\(_3\) in its \(3E\) state does undergo a Jahn–Teller distortion from \(D_{3h}\) to \(C_{3v}\)\(^2\), which leads to a bent Au\(_3\)(\(3A'\)) structure. The question is whether \(\sigma\)-electron delocalization is also observed in this case.

Investigation of acyclic Au\(_3\)(\(3A'\)) leads to a BSO value of 0.746 that suggests a 3e delocalization of the Au 6s electrons and its periphery and in line with its symmetry properties; Figure 2). The NICS(1) values for each of the 3-ring units are listed in Table 2). The NICS(1) values for each of the 3-ring units are listed in Table 2. The NICS(1) values for each of the 3-ring units are listed in Table 3. They reveal that NICS(1) values decrease with increasing annelation and decreasing positive charge of an Au\(_3\) ring. For the Au\(_4\) units in Au\(_3\)\(_n^+\), Au\(_4^+\) (in total five different Au\(_4\) rings in different clusters, called a@Au\(_4\), etc.) an exponential decay of NICS(1) with the parameter of the number of shared edges in a polycyclic structure (\(n_{\text{share}}\)) can be observed suggesting a decrease of aromatic \(\sigma\)-delocalization for the inner rings (Figure 3).

Free Au\(_3^+\) possesses the most negative NICS(1) value (−14.1 ppm) in line with its positive charge and the optimal 2e-delocalization. In Au\(_5^+\), the central ring a shares one edge with each adjacent Au unit. In this case, the NICS(1) value of ring b is reduced to −11 ppm, whereas that of ring a is lowered to −9 ppm. Defining the number of the shared edges by the parameter \(n_{\text{share}}\), the NICS(1) values vary from −9 ppm (\(n_{\text{share}}\) = 3) to −8 ppm (\(n_{\text{share}}\) = 2). This trend is qualitatively maintained for Au\(_7^+\) (Table 3) and reminds of the tendency of \(\pi\)-aromatic polybenzoides to prefer the structure with the largest number of aromatic sextets according to the Clar’s rule\(^63,75\). The Clar’s rule has also been used for inorganic BN analogues of polybenzenoid hydrocarbon systems.

In this sense, the value of \(n_{\text{share}}\) might be used to explain the relative low stability of isomers of the nonplanar Au\(_3\) and Au\(_4\) clusters. For Au\(_4\)(\(T_{d}\)), \(n_{\text{share}}\) has a value of 6 that is larger than

| molecule (sym) | bond | \(r\) | \(\kappa^2\) | BSO
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<tbody>
<tr>
<td>Au(<em>3^+)((D</em>{3d}))</td>
<td>Au–Au</td>
<td>2.705</td>
<td>0.833</td>
<td>0.610</td>
</tr>
<tr>
<td>Au(<em>3^+)((D</em>{3d}))</td>
<td>Au–Au</td>
<td>2.750</td>
<td>0.785</td>
<td>0.577</td>
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<tr>
<td>Au(<em>3^+)((C</em>{3v}))</td>
<td>Au1–Au2</td>
<td>2.640</td>
<td>1.032</td>
<td>0.746</td>
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<td>Au(<em>3^+)((C</em>{3v}))</td>
<td>Zn–Au</td>
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<td>Au1–Au2</td>
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<td>0.462</td>
<td>0.350</td>
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<td>Au1–Au3</td>
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<td>Au1–Au3</td>
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<td>0.593</td>
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<td>Au2–Au3</td>
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<td>0.846</td>
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<td>Au(<em>3^+)((C</em>{3v}))</td>
<td>Au1–Au2</td>
<td>2.693</td>
<td>0.934</td>
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<tr>
<td>Au2–Au3</td>
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<td>Au5–Au7</td>
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<tr>
<td>Au6–Au7</td>
<td>2.756</td>
<td>0.592</td>
<td>0.442</td>
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Table 2. Bond Distances \(r\) (Å), Local Force Constant \(\kappa^2\) (mdyn/Å), and BSO Values \(n\) for the Gold Clusters Investigated

| molecule (sym) | bond | \(r\) | \(\kappa^2\) | BSO
<table>
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<td>0.746</td>
</tr>
<tr>
<td>Au(<em>3^+)((C</em>{3v}))</td>
<td>Zn–Au</td>
<td>2.640</td>
<td>0.230</td>
<td>0.182</td>
</tr>
</tbody>
</table>

Table 3. They reveal that NICS(1) values decrease with increasing annelation and decreasing positive charge of an Au\(_3\) ring. For the Au\(_3\) units in Au\(_3\)\(_n^+\), Au\(_4^+\), and Au\(_5^+\) (in total five different Au\(_4\) rings in different clusters, called a@Au\(_4\), etc.) an exponential decay of NICS(1) with the parameter of the number of shared edges in a polycyclic structure (\(n_{\text{share}}\)) can be observed suggesting a decrease of aromatic \(\sigma\)-delocalization for the inner rings (Figure 3).

Free Au\(_3^+\) possesses the most negative NICS(1) value (−14.1 ppm) in line with its positive charge and the optimal 2e-delocalization. In Au\(_5^+\), the central ring a shares one edge with each adjacent Au unit. In this case, the NICS(1) value of ring b is reduced to −11 ppm, whereas that of ring a is lowered to −9 ppm. Defining the number of the shared edges by the parameter \(n_{\text{share}}\), the NICS(1) values vary from −9 ppm (\(n_{\text{share}}\) = 3) to −8 ppm (\(n_{\text{share}}\) = 2). This trend is qualitatively maintained for Au\(_7^+\) (Table 3) and reminds of the tendency of \(\pi\)-aromatic polybenzoides to prefer the structure with the largest number of aromatic sextets according to the Clar’s rule\(^63,75\). The Clar’s rule has also been used for inorganic BN analogues of polybenzenoid hydrocarbon systems.

In this sense, the value of \(n_{\text{share}}\) might be used to explain the relative low stability of isomers of the nonplanar Au\(_3\) and Au\(_4\) clusters. For Au\(_4\)(\(T_{d}\)), \(n_{\text{share}}\) has a value of 6 that is larger than
explaining the lower stability of the former that is also a saddle planar Au clusters investigated. The same holds for the energy, which is 6 for Au7 (Table 2), the properties of the electron density distribution at the RCP in the form of the Laplacian of \( \rho \).

The investigation of larger planar clusters becomes larger, suggesting the decrease of aromaticity or instability of the planar structures of Au. However, it is relevant how strong RCPs are shifted away from the geometrical center of a ring toward one of the bonds. This gives an area reflecting the extent of surface delocalization (see text). The Laplacian of \( \rho \) is given in e/bohr\(^2\), and \( \eta \) is in bohr\(^2\).

\( n_{\text{hare}} = 1 \) for Au4 (\( D_{2h} \)) thus suggesting that the latter is more stable. The nonplanar Au4 (\( T_d \)) cluster turns out to be a saddle point of first order at the B3LYP level of theory. Similarly, \( n_{\text{hare}} \) is 6 for Au6 (\( D_{3h} \)), whereas it is just 4 in Au7 (\( C_{2v} \)), again explaining the lower stability of the former that is also a saddle point rather than a minimum. In other cases, the \( n_{\text{hare}} \) value can be used to predict qualitative trends (see Table 3: Au7). It can be expected that the value of \( n_{\text{hare}} \) increases when the size of planar Au4 clusters becomes larger, suggesting the decrease of \( \sigma \)-aromaticity or instability of the planar structures of Au4. The energy difference between the planar and nonplanar structures will be decreased with the increasing of the cluster size, rationalizing the tendency that planar Au4 clusters are no longer stable for larger \( m \). The investigation of larger planar clusters is currently performed in our laboratories.

In general, both NAE and NICS(1) provide a measure too crude to correctly predict the relative stability of the neutral and cationic Au clusters investigated. The same holds for the energy gap \( \Delta \varepsilon \) and the ELF-\( \sigma \) values. The latter are almost the same for all clusters (Figure 1). Therefore, other properties of the clusters were investigated, which relate to their electron density distribution and vibrational modes.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>AI</th>
<th>electrons</th>
<th>( R ) or ( t_0 )</th>
<th>( k^2 ) (R)</th>
<th>( q(t_0) )</th>
<th>( k^2 ) (( t_0 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au4(^+)</td>
<td>0.553</td>
<td>1.084</td>
<td>0.079</td>
<td>4.213</td>
<td>0.036</td>
<td>2.135</td>
</tr>
<tr>
<td>Au6</td>
<td>0.835</td>
<td>1.827</td>
<td>0.037</td>
<td>5.793</td>
<td>0.092</td>
<td>1.833</td>
</tr>
<tr>
<td>Au5Zn(^+)</td>
<td>0.891</td>
<td>0.902</td>
<td>1.852</td>
<td>0.046</td>
<td>0.092</td>
<td>1.880</td>
</tr>
<tr>
<td>Au4, Au5Zn(^+)</td>
<td>1.224</td>
<td>1.492</td>
<td>0.046</td>
<td>0.092</td>
<td>1.880</td>
<td>0.092</td>
</tr>
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<td>1.880</td>
<td>0.092</td>
</tr>
</tbody>
</table>

The former competes for the electrons of the central bond. If these are unstable and can be stabilized either by rectangular or rhombic distortion. The square form of Au4 is Jahn–Teller unstable and can be stabilized either by rectangular or rhombic distortion. The latter leads to a planar bicyclic form with two 3-rings in which the four 6s(Au) electrons avoid peripheral delocalization and Jahn–Teller destabilization as much as possible as documented by a peripheral AI of 0.725. \( D_{3h} \) Symmetrical Au4 is best described as a central Au4 unit that donates some negative charge to the two apical Au atoms (see NPA values in Figure 2). To avoid the less stable 3c-3e bonding situation of the 3-ring the apical bond lengths are weakened (BSO: 0.350, Table 2), and \( \sigma \)-delocalization is suppressed. Note that the AI(a) value of 0.807 is misleading insofar as both 3-rings compete for the electrons of the central bond. These are...
split up (by dividing the BSO value by 2), an AI value of just 0.722, like the peripheral delocalization of 0.725, is obtained. Consequently, the absolute NICS(1) value of Au4 is with $|\Delta NICS(1)|$ extremely low (Table 3). At the RCP (which is removed from the central bond; see Supporting Information) the degree of surface delocalization is small as indicated by a compact delocalization region ($\eta = 1.619$ bohr$^2$, smallest value for all 3-rings investigated, Table 3), which is typical of a slightly positively charged central bond attracting two apical negatively charged Au atoms. This is in line with a low NAE value of just 33.6 kcal/mol (CCSD(T), Table 1). Noteworthy is that the positive charge of the bridge atoms reduces their covalent radius so that the Au1−Au3 distance becomes shorter.

If one scales the BSO values so that they add up to the number of $\sigma$-type valence electrons of Au$_m$ (note that this leads to a loss of the comparability of local force constants and BSO values between different metal clusters), one obtains 2e for the Au−Au bridge of Au$_4$ and 2e for the four bonds connecting the apical Au atoms to the bridge. The four apical bonds have only slight concave character (i.e., there is no $\pi$-complex character$^{54,55}$), which confirms that bonding in the Au$_m$ clusters is different from what is known from organic systems having the possibility of involving $\pi$-orbitals.

The analysis of the electronic structure of Au$_4$ reveals that the equilateral Au$_4$(3e) units in a polycyclic system prefer to distort. In $T_d$-symmetrical Au$_4$, symmetry and the polycyclic structure freeze the molecule in four unstable, equilateral 3c-3e units, which are prevented in the more stable rhombic $D_{2h}$-symmetrical form. Apart from this, the $T_d$-symmetrical Au$_4$ or the $D_{6h}$-symmetrical Au$_7$ cluster with its six destabilized 3c-3e units can only distort by ring breathing, that is, a concerted bond lengthening, and an overall weakening of the structure without effectively stabilizing the structure. This clarifies the chemical basis of the parameter $n_{share}$: polycyclic Au$_m$ structures with high symmetry and a large $n_{share}$ parameter enforce equilateral Au$_4$(3e) units and therefore cause instability.

In passing we note that the $D_{2h}$-symmetrical Au$_4$ cluster can be stabilized by opening one of the 3-rings and forming a more stable $C_{2v}$-symmetrical structure for which it is easier to realize a 3c-2e unit.

Au$_5$ ($^{2}A'$, $C_{2v}$). The ground state is a doublet radical with five 6s electrons that is characterized by a peripheral AI of 0.946,
whereas Al(a) = 0.553 and Al(b) = 0.770. Au<sub>4</sub> can be viewed as two overlapping Au<sub>4</sub> units with a common central ring a, so that Au1 and Au5 are both apex atom and bridge atoms at the same time (Figure 2), which leads to an effective atomic charge close to zero (0.030e; Figure 2). The bridge bonds Au1−Au3 and Au3−Au5 become labialized (BSO 0.223) because of a strong electron deficiency resulting from the fact that seven Au−Au bonds must be formed with just five electrons corresponding to 65% electron deficiency (9e of 14e are missing; Au4: 6e of 10e, i.e., 60% deficiency). Scaled BSO values reveal that there is effectively just one electron in ring a and two electrons in each ring b (Table 4). Peripheral electron delocalization involving somewhat more than 4.2e is preferred.

Aromatic σ-delocalization is stronger in ring b (AI = 0.770) than in ring a (AI = 0.553, Table 4), in line with the Clar's rule for gold clusters (generation of largely independent 3c-2e units similar to the situation of 6c-6e π-units in phenanthrene<sup>53</sup>) and the NICS results. The surface delocalization values are comparable in b (1.684 bohr<sup>2</sup>) and in a (1.688 bohr<sup>2</sup>, Table 3). They are slightly larger than in the reference molecule Au<sub>5</sub>, thus indicating a somewhat increased tendency of surface delocalization because of the symmetry and topology of the bonding network.

The stability of two largely independent 3c-2e units in Au<sub>4</sub> (topologically not possible in Au<sub>4</sub>) is confirmed by the increased NAE value (CCSD(T): 36.9 kcal/mol as compared to just 33.6 kcal/mol in Au<sub>4</sub> Table 1). The extra stability of Au<sub>4</sub> can also be documented by the breathing force constants<sup>66</sup> \(k'(R)\), which for ring b@Au<sub>4</sub> are significantly larger than those at ring a@Au<sub>4</sub> but smaller compared to the corresponding Au<sub>4</sub> value (breathing force constant, b@Au<sub>4</sub>: 5.172 mdyxn/Å; Au<sub>4</sub>: 7.533 mdyxn/Å, Table 4). Ring b@Au<sub>4</sub> can easily be distorted to avoid the unstable 3c-3e situation (distortion amplitude \(t_1 = 0.059\) Å, distortion force constant \(k'(t_1) = 1.592\) mdyxn/Å, Table 4), which is more difficult for a@Au<sub>4</sub> (\(t_1 = 0.036\) Å; \(k'(t_1) = 3.801\) mdyxn/Å, Table 4), as the latter has only the possibility of moving the apex atoms away from the bridge Au1−Au3, which leads to dissociation.

\[ Au_6(\text{Ar}_5, D_{3h}) \] If another Au atom is added to Au<sub>4</sub> then the most stable structure of Au<sub>6</sub> is formed as a planar \(D_{3h}'\) symmetrical cluster with three largely independent 3c-2e units and a central ring a that has a positive charge of +0.3 e (NBO value) and long, weak bonds (2.901 Å, BSO: 0.262). Scaled BSO values suggest that just 0.520e (Table 4) are forming the central ring. Its AI is relatively low (0.506) as is its breathing constant of 3.525 mdyxn/Å (Table 4).

Ring b has stronger bonds (BSO: 0.625) and contains (after scaling) 1.827e in line with the ideal 3c-2e situation. Accordingly, both its AI and \(k'(R)\) value are high: 0.835 and 5.793 mdyxn/Å. The three rings a form a peripheral six-bond Au<sub>6</sub> triangle with the perfect AI value of 0.999 (Table 4). Since the stabilities of the peripheral Au<sub>6</sub> triangle and the three peripheral rings dominate the overall stability of the cluster, the NAE value of 43.1 kcal/mol is even somewhat larger than that of Au<sub>5</sub> (42.5 kcal/mol; Table 1).

\[ Au_7(\text{Ar'}_3, C_2v) \] Adding another Au atom to Au<sub>6</sub> leads to Au<sub>7</sub>, which in its most stable form has five different 3-rings. These can be viewed as being formed from a bicyclic Au<sub>6</sub> unit (rings a and b) with three peripheral 3c-2e-rings c, d, and e. The AI values (0.352 (a), 0.542 (b), 0.848 (c), 0.882 (d), 0.854 (e)) are similarly ordered as the \(t_0 = R - R_0\) or \(k'(R)\) values: 0.134 (a), 0.091 (b), 0.038 (c), 0.027 (d), 0.037 Å (e) and 2.049 (a), 2.174 (b), 6.024 (c), 6.512 (d), 5.912 mdyxn/Å (e). This suggests a decreased stability (increased breathing deformation) in the series \(d ≈ e > c ≫ b ≫ a\) in line with the 3c-2e Clar's rule for Au<sub>4</sub>.

For all Au<sub>5</sub> investigated, bridge Au atoms have positive NPA charges, whereas apex atoms have negative charges (Figure 2). This is also the case for rings d (--0.062), e (--0.093), and c (--0.063 e) in Au<sub>7</sub>. Scaled BSO values suggest that ring d is closest to the ideal 3c-2e situation (2.010 e), followed by rings e (1.838), c (1.502), b (1.166), and a (0.484 e). These observations are in line with the 3c-2e Clar's rule, the NICS values, and an NAE value of 45.3 kcal/mol (compared to 46.1 kcal/mol for Au<sub>4</sub> PBE06-D3(BJ), Table 1), which results of course from the stability of three external relatively stable 3-rings.

\[ Au_5Zn^+(\text{Ar}_1, C_2v) \] This molecule has been previously described as a σ-aromatic system. It is now means the to quantify this description by comparing with Au<sub>5</sub>Zn<sup>2+</sup> as a reference ion. The latter has an AI of 0.992; that is, it is also a σ-aromatic 3c-2e system. It is a suitable reference system to analyze Au<sub>5</sub>Zn<sup>+</sup>. For this purpose, eq 2 was reparametrized to obtain reasonable AI values (see Supporting Information). The three peripheral rings of Au<sub>5</sub>Zn<sup>+</sup> have AI values of 0.929 (b) and 0.826 (c), whereas ring a has an AI of just 0.474. This again indicates a large degree of σ-delocalization because of the positive charge, which is distributed over the atoms of rings a and c: Au1 (0.113), Au2 (0.051), Zn4 (0.874e, Figure 2). The bonds involving Zn become stronger (BSO values of 0.751 and 0.425 vs 0.625 and 0.262 in Au<sub>5</sub>, Table 2), which is because of the higher electronegativity of Zn (Pauling scale: 1.65 vs 1.42 for Au) especially in view of its high positive charge.

Theoretically, when splitting up charges always equally, the six valence electrons could be equally distributed among rings c, 2 × b, and a: 1.666; 1.666; 1.666; 1.000. The NPA charge distribution gives ratios of 1:519:1:737:1:737:1:007 thus suggesting that ring c loses charge that is drawn into the two rings b and to the more electronegative Zn atom (at Zn the charge is reduced from +1 to 0.874e) and Au3 as well as Au5 (−0.04se). The charge of ring a does not change much so that this ring is just a means for the charge flow from Au1 to the base.

Since the covalent bonding radius of Zn<sup>+</sup> is much smaller than that of Au or Au<sup>+</sup>, the \(D_{3h}'\)-symmetrical triangle of Au<sub>6</sub> becomes a \(C_{2v}\)-symmetrical structure with inwardly bent Au3−Zn4−Au5 unit (see bond path diagram in Supporting Information) so that Zn<sup>+</sup> is "inside" the ring structure and bonds are much stronger. Both the AI (Table 4) and NICS(1) values (Table 3) confirm strong σ-delocalization: b (−12.6) < c (−11.9) < a (−10.0 ppm, Table 3). Au<sub>5</sub>Zn<sup>+</sup> is more stable than the valence isoelectronic Au<sub>5</sub>, as is confirmed by a high NAE value of 49.4 kcal/mol (CCSD(T), Table 1).

The optimal form of Au<sub>5</sub>Zn<sup>+</sup> must contain Zn in a central rather than apical position. Only in this way is the delocalization of some of the positive charge limited to rings a and c and leaves the apical atoms Au3 and Au5 negatively charged. The deformation force constants confirm the order of ring stabilities (Table 4) and, together with AI and NICS values, predict Au<sub>5</sub>Zn<sup>+</sup> as an exceptionally stable σ-aromatic cation.

4. CONCLUSIONS

Gold clusters have a strong tendency to adopt structures built from 3-ring units. This is a direct result of the extra stability of the Au<sub>5</sub> (2e) unit, which benefits from σ-electron delocalization.
partially caused by scalar relativistic effects. Adding another electron to obtain the neutral $\text{Au}_n(3e)$ leads to a Jahn–Teller unstable system, which must distort to gain stability. This is most pronounced in polycyclic structures because of the difficulty of distorting a highly symmetric structure in an effective way. Examples are the $T_d$-symmetrical $\text{Au}_4$ or the $D_{5h}$-symmetrical $\text{Au}_5$ that are both stationary points of cluster rearrangements. The $D_{5h}$-symmetrical $\text{Au}_5$ can better distort, however, for the price of a relatively small peripheral AI value leading to a central $\text{Au}_2$ unit attracting two apical Au atoms.

AI, NICS, and deformation parameters suggest a simple building principle for small $\text{Au}_n$ clusters that is closely connected to the relative stabilities of $\text{Au}_4(3e)$ and $\text{Au}_4(3e)$ systems. If a 3-ring can be converted into a unit adopting some features of the $\text{Au}_4(3e)$, stability will be achieved by $\sigma$-aromaticity. For the small $\text{Au}_n$ clusters investigated, a distorted 3-ring is always possible if three-dimensional clusters are avoided. In the two-dimensional structures, the use of 3-rings as building blocks leads to a steep increase in the number of bonding interactions that require electron-deficient bonding. This in turn enforces electron sharing between 3-rings and a move of negative charge from the more central 3-rings to the peripheral 3-rings so that the latter can adopt 3c-2e units of larger stability with relatively strong bonding on the outside and weak (electron-deficient) Au–Au bonds on the inside. This is correctly predicted by the vibrational properties of these molecules in the form of the local stretching force constants, their associated BSO values, and the AI that measures the degree of $\sigma$-electron delocalization.

The results of this work can be a basis to predict the stability of larger gold clusters, which no longer might prefer a planar structure. Besides the Clar’s rule for 3-rings, one must consider stabilization via peripheral electron delocalization and the avoidance of other highly destabilized subunits such as the tetracyclic and bicyclic $\text{Au}_4$ or the hexacyclic $\text{Au}_4$ unit. Work is in progress to provide a general rationale for the stability of larger gold clusters.

$\pi$-Aromaticity has been described as a multidimensional problem,¹³ which means that by measuring different properties of an aromatic molecule different manifestations of aromaticity are obtained. The same holds for $\sigma$-aromaticity: (i) Energetic properties reveal the impact of aromaticity on the molecular stability. (ii) The electron density distribution and its Laplacian provide an insight into the spatial extension of aromaticity (one-, two-, or three-dimensional delocalization). (iii) Vibrational force constants reflect via BSO and AI the bond strength and the degree of electron delocalization. (iv) Magnetic properties such as the NICS values are the basis for a hypersensitive measure of magnetic anisotropy and potential orbital currents. Since the energy is a robust but very insensitive measure and the magnetic properties are too sensitive indicating even the weakest delocalization effects, the AI based on local stretching force constants seems to be the most useful measure, especially if it is combined with electron or energy density properties: In this way, a sensitive but not too sensitive measure of electron delocalization is obtained, by which one can distinguish local and global electron delocalization.

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**REFERENCES**


Aromaticity in an unsaturated ring: osmapentalene derivatives

ring strain, and surface delocalization.

σ measurements versus density functional calculations.

cyclopropane and cyclobutane


(43) Peterson, K.; Puzzarini, C. Systematically convergent basis sets for transition metals. II. Pseudopotential-based correlation consistent basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements. Theor. Chem. Acc. 2005, 114, 283–296.


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