Tetrahedral $\text{Au}_{17}^+$: A Superatomic Molecule with a $\text{Au}_{13}$ FCC Core

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Supporting Information

ABSTRACT: A unique tetrahedral structure of $\text{Au}_{17}^+$ ($T_d$) is found by using first-principles global optimization, which lies 0.40 eV lower in energy than the previously known structure and has a fairly large HOMO–LUMO gap (1.46 eV) at the TPSS/def2-TZVP level. For neutral $\text{Au}_{17}$, this tetrahedral structure is distorted to $D_{4d}$ symmetry but is also 0.18 eV lower in energy than the previous flat cage structure. $\text{Au}_{17}^+$ ($T_d$) has a FCC $\text{Au}_{13}$ octahedral core, and the other four gold atoms are above its four triangular faces. Magic electronic stability of the cluster is explained by the super valence bond model, of which it can be seen as a superatomic molecule in the electronic structure. Moreover, the cluster can also be viewed as a network of eight 2e-superatoms. This $\text{Au}_{17}^+$ cluster mimics the behavior of the $\text{Au}_{20}$ pyramid, known as a unique one among the family of gold clusters since its discovery in 2003, in electronic structures.

1. INTRODUCTION

Gold clusters and nanoparticles have been a hot issue during the past few years due to their particular properties, such as the unique size-dependent catalytic activity, relativistic effects, aurophilic attraction, and hyperfine properties, 1–2 and many experimental and theoretical investigations surged on this aspect. 3–6 Due to the strong relativistic effects, Au clusters have very unique geometric properties compared to other coinage metals. Small Au clusters display unique planar structures at about $n = 2–10$, 7,8 a transition from 2D to 3D structures at $n = 11–13$, 9,10 flat cage at $n = 14–19$, 11–13 pyramidal cage for $\text{Au}_{20}$, 14 golden fullerene for $\text{Au}_{20}$, 15–16 and the core–shell structure at $n = 33–38$. 17 Similar 2D-to-3D structural transitions are also viewed for Au cluster cations and anions, but the transition sizes are different. 3–6

Electronic shells of metallic clusters can be understood by the Jellium model, 18,19 which assumes a uniform background of positive charge of the cluster’s atomic nuclei and the innermost electrons, in which valence electrons move and are subjected to an external potential. Thereby, the whole cluster can be viewed as a “superatom”. The appropriate aufbau rule of super shells for spherical Au clusters is [1S1P61D10]2S21F14, etc., associated with magic numbers 2, 8, 18, 34, etc. 20

Among Au clusters, $\text{Au}_{20}$ is very unique in geometry, 14 which possesses a pyramidal structure ($T_d$) and is a small piece of the face-centered-cubic (fcc) lattice of bulk gold at a small relaxation. It has a remarkably large energy gap (1.77 eV) between the highest occupied and lowest unoccupied molecular orbitals (H–L), suggesting high electronic stability. The full-filled 5d electrons of Au (5d106s1) are mainly localized as lone-pairs (LPs) and 6s2 are free valence electrons, and there are 20 free electrons in $\text{Au}_{20}$ which, however, does not follow the magic number (18e) in the spherical Jellium model.

To understand the magic stability of the $\text{Au}_{20}$ pyramid, King et al. 21 thought that the 20 free electrons can be used to form a 4-center 2-electron (4c–2e) bond in each of the 10 tetrahedral cavities of the $\text{Au}_{20}$ cluster (four at the vertices and six at the edges). Later, such a conjugated 4c–2e bonding model was confirmed by chemical bonding analysis. 22 $\text{Au}_{20}$ can also be viewed as a network of ten 2e-superatoms (10 × 2e) based on the superatom-network (SAN) model. 23 More recently, based on the newly proposed super valence bond (SVB) model, 24–26 $\text{Au}_{20}$ is proven to be a superatomic molecule bonded by one 16c–16e $\text{Au}_{16}$ superatom and four Au atoms. 27

Since the discovery in 2003, 14 the $\text{Au}_{20}$ pyramid is taken as an exception different from any other Au clusters. However, in this work, we find a sister of it by using density functional theory (DFT) calculations: tetrahedral $\text{Au}_{17}^+$ cluster. It is analogous to $\text{Au}_{20}$ in electronic properties and can be viewed as a superatomic molecule based on the SVB model.

2. COMPUTATIONAL METHODS

The structures are located by unbiased global search of the potential energy surface using the genetic algorithm (GA) 28–30 at the DFT level. DFT calculations are carried out on Gaussian 09 package, 31 using the generalized gradient approximation method by Tao–Perdew–Staroverov–Scuseria (TPSS) 32 with relativistic effective core potential basis set (def2-TZVP). The
calculated H-L gap (1.91 eV) of Au$_{20}$ pyramid at the TPSS/def2-TZVP level is in good agreement with the experimental value (1.77 eV).14

3. RESULTS AND DISCUSSION

Tetrahedral Au$_{17}^+$ (I) also has a high $T_d$ symmetry and has an octahedral Au$_{13}$ core. The Au$_{13}$ octahedron is a FCC fragment, which has six square faces and eight triangular faces. The other four gold atoms are above the non-nearest neighbor triangles (Figure 1). The calculated H-L gap of the tetrahedral Au$_{17}^+$ is also fairly large (1.46 eV), indicating high electronic stability. The other nine low-energy isomers (II-IX) located in the unbiased global search are plotted in Figure 2a, which are 0.40−0.60 eV higher in energy. Isomer X is based on the Au$_{20}$ pyramid, which is not located in the unbiased search due to its high energy (0.91 eV). It should be noted that the structures and their energetic order of gold clusters are very sensitive on the functional, and it was found that the TPSS functional agrees well with the high level coupled cluster method for small charged Au clusters.33,34 The high level wave function method cannot be performed due to the large size of the current system. However, for each DFT methods with and without dispersion interaction, isomer I is the energy lowest one (Table S1).

Experimentally, the information on cluster structures cannot be given directly, but some physical properties are measured by ion-mobility or trapped ion electron diffraction methods, and the structural information is deduced from the comparison of the simulated values from DFT-predicted structures and the experimental values.5,6,35 Previously, isomer IV is found in maximal agreement with the experimental data in simulated and experimental reduced molecular scattering functions.35 However, isomer I is not successfully predicted in previous works and is even 0.54 eV lower in energy than isomer IV. To further verify the newly predicted tetrahedral cluster, energies of isomers I and IV are compared by the wave functional method, and I is 0.59 eV lower in energy than IV at the MP4/def2-TZVP level of theory.

For comparison, the low-energy isomers for neutral Au$_{17}$ clusters are also located using the GA-DFT method as plotted in Figure 2b. In the neutral state, the tetrahedral cluster is changed to a $D_{2d}$ symmetry (a) due to Jahn–Teller distortion. Interestingly, the previously reported global minimum structure for neutral Au$_{17}$ is (b) a flat cage structure,11 which is 0.18 eV higher in energy than the tetrahedral structure at the TPSS/def2-TZVP level [using the same PBE/LANL2DZ method as in ref 11, isomer a is also 0.12 eV lower in energy than isomer b]. All the isomers are verified to be real local minima by frequency check.

The low energy, large HOMO−LUMO gap, and high symmetry suggest the magic stability of structure I to be similar to Au$_{20}$. Here we first explain the magic electronic stability of I by using the SVB model. The octahedral Au$_{13}^+$ core of I is spherical enough and can be viewed as an open-shell 12e-superatom (abbreviated as O). Electronic shells of O (1S$^2$1P$^6$1D$^4$) follow the rule of the spherical Jellium model. Molecule-like electronic shell-closure is achieved by four superatom−atom super bonding (O−Au), and I can be viewed as a superatomic molecule OAu$_4$. Figure 3 gives a schematic representation of the bonding pattern of OAu$_4$. The 1S$^2$1P$^6$...
shells of O are super LPs. The five 1D orbitals split into two sets in a tetrahedral field, a set of double-degenerate orbitals (1D,2−2y2,2z2) and a set of triple-degenerate orbitals (1D,2−2z2,2x2). The two 1D,2−2z2 orbitals are empty. The three 1D,2−2y2 orbitals are in D, S hybridization with the 2S orbital. The four D, S super orbitals are bonded with four 6s1 orbitals of the vertexal Au atoms, splitting into four occupied lower bonding orbitals and four higher antibonding orbitals. Such a bonding pattern is analogous of a simple molecule TiH4, where Ti [3s23p6(3d4s)4] is in d’s hybridization bonded with four H atoms.

The comparison of Kohn–Sham molecular orbital (MO) diagrams of OAu4 and TiH4 are given in Figure 4. It is clearly shown that they have similar electronic configurations and orbital shapes. The 1S1P orbitals of superatom O and 3s3p orbitals of atom Ti correspond to (1a1)2(1t2)6 MOs. The unoccupied 1D,2−2y2,2z2 orbitals of O and 3d,2−2y2,2z2 orbitals of Ti correspond to (1e)0 MOs. The four D, S-6s, d, s-1s of O–Au and O–H bonding orbitals correspond to (2a1)2(2t2)6 MOs, while the four antibonding orbitals are (3a1)0(3t2)0 (3a1)0 (3t2)0 MOs, respectively.

To further confirm the existence of superatom–atom super bonding in I (OAu4), we investigate its chemical bonding patterns using the adaptive natural density partitioning (AdNDP) method. As shown in Figure 5, AdNDP chemical bonding analysis reveals four 13c−2e super LPs in O (super 1S1P) and four 14c–2e super O–Au σ-bonds (D3S-s), with very high occupancy numbers (ONs > 1.98|e|). As a comparison, a similar bonding pattern of the simple molecule TiH4, where Ti–H is bonding in d’s-s hybridization, is also shown.

Under the framework of the SVB model, the superatom–atom bonding in I (OAu4) is very similar to that of Au20 (TAu4), where superatoms O and T are both in D, S hybridization. The difference is that the super 1D,2−2y2,2z2 orbitals are occupied in T but are unoccupied in O. Besides, similar to Au20, electronic structure of the tetrahedral Au4, also follows the SAN model. As shown in Figure 6, the 16 free electrons can be used to form a 4c−2e bond in each of the 8 tetrahedral cavities of I (4 at vertices and 4 at the body). Thus, the whole cluster can be viewed as a network of eight 2e-superatoms (Au4 tetrahedron). The vertexal tetrahedron is composed of one vertex Au atom and three Au atoms in one triangular face of the Au13 core. The inner tetrahedron is composed by one central Au atom and three Au atoms in one triangular face. The four inner tetrahedrons share one central Au atom. Each vertex tetrahedron shares three Au atoms with three inner tetrahedrons.

On the basis of the above geometric analysis, there are two kinds of conjugated 4c–2e Au4 superatoms (vertexal and inner) existing in Au20. AdNDP analysis conforms to such a 8 × 2e SAN model, which reveals eight delocalized 4c–2e σ bonds as shown in Figure 6. ONs of the 4c–2e bonds in vertices are 1.84|e|, while ONs of the inner 4c–2e bonds are 1.75|e|.

To further verify the 8 × 2e SAN model, the nucleus-independent chemical shifts (NICS) values at the center of the Au4 tetrahedron are calculated. NICS value is a popular measurement of aromaticity, where large negative value denotes aromaticity. NICS values of the vertexal and inner tetrahedrons are −12.73 and −16.63 ppm, respectively, showing high aromaticity. There is also another kind of Au4 tetrahedrons in...
I, which is composed by a triangular face of the vertexal Au tetrahedron and the central Au atom. However, its aromaticity is obviously lower according to NICS values (−7.70 ppm).

On the one hand, the higher aromaticity in the eight Au4 superatoms indicates certain localization of the electronic density (SAN model). On the other hand, the aromaticity of the nonsuperatom Au12 tetrahedrons is also fairly high, indicating certain delocalization of the electronic density in the whole Au13 octahedron (SVB model). Both SVB and SAN models can give reasonable understanding of the electronic stability of the Au20 and Au17+ clusters. The relationship between SVB and SAN models can be understood by the electronic structure of benzene. The SVB model corresponds to the model of 6c-6e delocalized π bonding, while the SAN model corresponds to the model of three conjugated 2c-2e π bonds. The two models are not in conflict with each other. The SVB model focuses on the delocalized multicentered bonding throughout the whole cluster, while the SAN models tend to the delocalized multicentered bonding between a part of the cluster, which can be viewed as a superatom. Then, the spherical symmetry or nearly spherical symmetry geometric structure of a cluster is needed in the SVB model, but this is usually not necessary in the SAN model. Sometimes, a cluster can be explained well in the SAN model yet not in the SVB model due to the whole geometric structure. In the SVB model, the ONs are close to the idealized value (2.0−), indicating high reliability. However, the fairly large ONs in the SAN model (1.75−I.84e) indicate certain localization of the 16 valence electrons. Thus, we think that, both models are reasonable, but the superatomic model gives more useful insight from the view of chemical bonding.

4. CONCLUSIONS

In summary, we find a unique structure of gold cluster cation \( \text{Au}_{17}^+ \) based on DFT calculations. This cluster is in \( T_d \) symmetry composed by an octahedral FCC Au13 core and four vertexal Au atoms. On the basis of the SVB model, Au17+ can be viewed as a superatomic molecule (\( \text{O} \text{Au}_4 \)) bonded by one 13c−12e superatom and four vertexal Au atoms, and it is an exact analogue of the \( \text{T} \text{H}_4 \) molecule. On the basis of the SAN model, eight 4c-2e superatoms are divided into two groups, alternately linking to each other, forming a network of tetrahedral 2e-superatoms. The tetrahalid \( \text{Au}_{17}^+ \) clusters is the only known sister of the famous Au19 pyramid, where the two clusters are similar in electronic structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b07917.

The calculated TD-DFT optical absorption spectra of tetrahedral \( \text{Au}_{17}^+ \) and Au20 clusters, comparison of various functionals in relative energies, and the xyz coordinates of the low-energy isomers of Au17+ and Au17 clusters (PDF)

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AUTHOR Contributions

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Notes

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