Geometry and Stability of Small Gold Cluster Ions by Graph Theory and Hückel model

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Abstract. Structure and stability of the gold cluster ions of which skeleton are synthesized as a complex were analyzed using the Hückel method based on graph theory. Hückel Energy (HE) and Topological Resonance Energy (TRE) were determined for neutral, positive ion, and negative ion clusters, where all the isomers of the gold cluster up to octamer were considered. Since some graphically designed isomers include bonds that cannot be realized in three-dimensional space, the screening was carried out by a molecular force field calculation with LAMMPS (lammps.sandia.gov/). Among the isomers thus obtained, both HE and TRE were most stable when the tetramer was Au$_2^{2+}$ with a tetrahedral structure, and with the hexamer, Au$_6^{2+}$ with two tetrahedrons sharing one side. The complexes with these structures have actually been synthesized. On the other hand, the synthesis example of the most stable cluster for octamer Au$_8$ has not been reported.

1. Introduction
The purpose of this study is to clarify the geometry characteristics and stability of gold clusters using graph theory and Hückel model. The reason why the Hückel method was chosen is that it is easy to perform calculations. Table 1 shows the number of isomers of clusters of several sizes [1]. The number of isomers increases rapidly as the number of atoms increases, and the number of isomers exceeds 10,000 for octamers. There are too many isomers to obtain precise result.

| n  | isomers | n  | isomers |
|----|---------|----|---------|
| 4  | 6       | 7  | 853     |
| 5  | 21      | 8  | 11,117  |
| 6  | 112     | 9  | 261,080 |

Although the calculation is relatively simple, the Hückel method is not considered bad for Na, Cu, and Au clusters that have one 1s electron in the outermost shell. Figure 1 shows the most stable structures of M$_3$ – M$_8$ clusters where M=Na [2], Cu [3] and Au[4] obtained by ab-initio or DFT calculation. The structures obtained by the Hückel method are the same as those for Na clusters, except for octamer. For Cu and Au clusters, the structures are almost the same with a few exceptions. From this comparison, it was considered a good approximation to discuss cluster stability using the Hückel method.
Various gold complexes have been synthesized so far [5-9]. The variety of isomers is abundant and ideal for comparison. This is the reason why we chose gold clusters in order to elucidate determining factor of the stability of metal cluster isomers.

2. Computational Methods

2.1. Adjacent Matrices

First, we create a list of all isomeric graphs by creating code in Mathematica or C++ [10,11]. The graph is represented by an adjacency matrix. Once we get adjacency matrix, Hückel Energy (HE) is automatically obtained by calculating the eigenvalues of the adjacency matrix. In this study, Topological Resonance Energy (TRE), that is a kind of aromatic stabilization energy, was also calculated. The procedure for obtaining TRE is quite complex, but it can be also obtained from the adjacency matrix. For a detailed description of TRE, see the review [12].

2.2. Elimination of Impossible Structures

Next, we will examine whether the stability of the complex actually synthesized can be explained from the values of HE and TRE. It is necessary to remove impossible isomers before examination. Some graphically designed isomers contain bonds that are not possible in 3D space. For example, it is impossible for K5 complete graph, where every atom is bonded to every other atom, to set all bond lengths are equal. We screened the isomers by molecular mechanics (MM) calculation with LAMMPS [13]. The screening procedure for removing impossible isomers is as follows. The atom is placed at the position corresponding to the given number. Bonds are created based on the adjacency matrix. Then the MM calculation is carried out, where

1) the bond potential is expressed using the Morse function,
2) set the angle function to be most stable at 180 degrees with harmonic oscillator approximation,
3) a repulsive force works between atoms which are not bonded.

The 3D-structure obtained in this way is defined as the most stable one corresponding to a given adjacency matrix (graph-structure). For the 3D-structures, we examined the distances of all atom pairs [14]. The judgement based on the distance between atoms is carried out as follows. If the bond atom pair distance is 0.9 $r_0$ to 1.1 $r_0$, where $r_0$ is the equilibrium internuclear distance, and if the distance between unbonded atom pairs is more than 1.1 $r_0$ simultaneously, this structure is permitted. A slightly relaxed condition, 0.85 $r_0$ and 1.15 $r_0$, is also used. After this screening, one pentamer, 13 hexamer, 207 heptamer and 5,079 octamer isomers are excluded, where the criteria are 0.9 $r_0$ and 1.1$r_0$. Figure 2
shows the screening results for octamer. Isomers that may exist in more severe conditions are shown in green. Clusters that cannot exist are shown in red. Isomers that can exist under relaxed conditions are shown in blue. The vertical axis is the value obtained by MM calculation of LAMMPS, and it shows that the stability increases as the value decreases. We can see that no octamer isomer with more than 20 bonds can exist.

![Figure 2](image.png)

**Figure 2.** Possible and impossible octamer isomers screened by LAMMPS. The bond atom pair distance \( r \) is compared with the equilibrium internuclear distance \( r_0 \).

Green: possible, \( 0.9 \ r_0 < r < 1.1 \ r_0 \). Blue: maybe, \( 0.85 \ r_0 < r < 0.9 \ r_0 \), \( 1.1 \ r_0 < r < 1.15 \ r_0 \). Red: impossible, \( r < 0.85 \ r_0 \), \( 1.15 \ r_0 < r \). The distance between unbonded atom pair was also examined, see the text.

3. Results and discussion

3.1. HE and TRE

We calculated not only neutral but also positive and negative ion clusters and compared HE and TRE values. Figures 3 and 4 show the mean values of HE and TRE, respectively, as a function of number of bonds in different charges for octamers. As shown in Fig. 3, the HE increases monotonously only when the charge is +6, and the others show the shape of a bowl rising to the right. Also, the smaller the charge, the more slowly it rises. It can be seen that the reversal of the HE occurs due to the increase in the number of bonds, and the charges +2, +4 are larger than the neutral and charge -2. Such a tendency was also seen in the tetramer, pentamer, hexamer and heptamer. As an overall trend, it can be said that HE increases as the charge becomes more positive and the number of bonds increases.

As shown in Fig. 4, the mean value of TRE takes a positive when the charge is +6, +4 or +2, and takes negative when the charge is neutral or negative. When examining each isomer, most of the TREs with positive values were +4 and +2.
Table 2 summarizes the HE and TRE values of isomers that have the same structure and charge as the synthesized complexes. When ranking, we excluded structures that could not be realized in 3D. Figure 5 shows skeletal structure of synthesized gold cluster. In Fig. 5, the most stable octamer isomers are also shown.

### 3.2. Comparison with synthesized clusters

Table 2 summarizes the HE and TRE values of isomers that have the same structure and charge as the synthesized complexes. Table 2 also shows how large HE and TRE are among the same charge isomers. When ranking, we excluded structures that could not be realized in 3D. Figure 5 shows skeletal structure of synthesized gold cluster. In Fig. 5, the most stable octamer isomers are also shown.

#### Table 2. HE and TRE values for the synthesized Au complexes. The alphabets and the numbers in the “complex” column correspond to that in Fig. 5 and the references, respectively.

| Cluster Size | Bonds | Charge | Complex               | HE/ | Rank | TRE/ | Rank |
|--------------|-------|--------|-----------------------|-----|------|------|------|
| 4            | 6     | +2     | $[^{15}B]_4$PAu$_4$]$_2$+ (a) [5] | 6.00 | 1    | 1.33 | 1    |
| 6            | 11    | +2     | $\text{Au}_6$(PPH$_3$)$_3$]$_2$+ (b) [6] | 9.66 | 1    | 0.76 | 7    |
| 6            | 10    | +2     | $\text{Au}_8$(dppp)$_4$]$_2$+ (c) [7] | 9.12 | 6    | 0.66 | 10   |
| 7            | 16    | +1     | $\text{Au}_7$(PPH$_3$)$_{1+}$ (d) [7] | 11.87 | 1    | -0.79 | 489 |
| 7            | 13    | +3     | $\text{Au}_7$(dppp)$_4$]$_2$+ (e) [8] | 11.13 | 7    | 1.53 | 8    |
| 8            | 12    | +2     | $\text{Au}_8$(PMe$_3$)$_6$]$_2$+ (f) [7] | 12.36 | 790  | 1.29 | 2    |
| 8            | 16    | +2     | $\text{Au}_8$(PPH$_3$)$_{1+}$ (g) [7] | 13.60 | 21   | 0.70 | 147  |
| 8            | 16    | +2     | $\text{Au}_8$(dppp)$_4$]$_2$+ (h) [7] | 12.47 | 646  | -0.47 | 4441 |
| 8            | 16    | +2     | $\text{Au}_8$(PPh$_3$)$_6$]$_2$+ (i) [9] | 12.52 | 580  | -0.36 | 3970 |
| 8            | 19    | +2     | Not synthesized (j) | 13.87 | 1    | -0.19 | 3047 |
| 8            | 13    | +2     | Not synthesized (k) | 13.09 | 142  | 1.31 | 1    |
| 8            | 15    | +4     | $\text{Au}_8$(dppp)$_4$Cl$_2$]$_2$+ (l) [7] | 12.17 | 88   | 2.00 | 45   |
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Figure 5. Skeletal structure of synthesized gold cluster. (a) tetramer. (b) and (c) hexamer. (d) and (e) heptamer. (f) – (i) octamer (+2). The most stable octamer (+2) isomer (j) in HE (k) in TRE. (l) octamer (+4). See also Table 2.

The most stable tetramer is shown in Fig.5 (a), which is tetrahedron, +2 ion isomer. Here both HE and TRE are the largest among the tetramer isomers. A complex with this isomer as a skeleton was synthesized in 1993 by Zeller et al. [5]. No other synthesis examples of gold tetramer were found.

Two types of Au complexes with hexamer skeletons are synthesized, shown in Fig.5 (b) and (c). The structure (b) consists of two tetrahedrons with sharing one edge, +2 ion clusters. Here HE is the largest and TRE is the 7th in all the hexamers. This complex was synthesized by Briant et al. in 1993 [6]. The complex (c) is recently synthesized [7]. Both HE (the 6th) and TRE (the 10th) shows that this isomer is relatively stable. As shown in Fig. 5 (d) and (e), two types again of Au complexes with a heptamer skeleton are synthesized [7,8]. As to isomer (d), HE is the largest. The isomer (e) has also large HE value. Figure 5 (f) – (i) shows synthesized complexes with heptamer skeleton, which have all +2 charge [7,9]. The TRE for isomer (f) and the HE for isomer (g) are relatively large but that is not the case for isomer (h) and (i). Furthermore, the complex with the most stable octamer isomer in HE (j) or that in TRE (k) has not been synthesized yet. Tsukuda states based on the shell model that the Au $^{2+}$ ion is a six-electron system and should be stable when it has a flat structure [15]. This may be the reason why isomers (h) and (i) are synthesized.

There is only one example of complex where the charge for the octamer skeleton is +4, as shown in (l). The HE and TRE values for this isomer is not small. It suggests that other complexes will be synthesized from the stability evaluated by the HE and TRE values.

4. Conclusion
For tetramer, hexamer and heptamer clusters, the gold complexes of which skeleton is the most stable isomer, based on HE, has been synthesized. The skeleton isomers of the synthesized complexes are also stable from the TRE perspective.
However, for octamers, there has been no report that the most stable complex in HE with the skeletal isomer has been synthesized. Many kinds of complexes with octamer skeleton have been synthesized, and their HE and TRE are not necessarily large. Other factors such as shell structure may affect the ease of synthesis of the complex.

References

[1] Y. Wang, T. George, D. M. Lindsay, and A. C. Beri, “The Hückel model for small metal clusters. II. Orbital energies, shell structures, ionization potentials, and extrapolation to the bulk limit”, J. Chem Phys., vol. 86, no.6, pp.3493-3499, 1987.

[2] I. A. Solov'yov, A. V. Solov'yov, and Walter Greiner, “Structure and properties of small sodium clusters,” Phys. Rev. A - At. Mol. Opt. Phys., vol. 65, no. 5, pp. 532031–5320319, 2002.

[3] D. Die1, B-X Zheng, L.-Q Zhao1, Q-W Zhu1 Z.-Q. Zhao, “Insights into the structural, electronic and magnetic properties of V-doped copper clusters: comparison with pure copper clusters,” Sci. Rep., vol. 6, no. 1, p. 31978, Aug. 2016. DOI: 10.1038/srep31978

[4] L. Rincon, A. Hasmy, M. Marquez, C. Gonzalez, J. Wu, S. Pan, X. Zhu, Z. Cai, P. Zhang, and C. Zhang, “A perturbatively corrected tight-binding method with hybridization: Application to gold nanoparticles”, Chem. Phys. Lett., vol. 503, no. 1–3, pp. 171-175, 2011, doi: 10.1016/j.cplett.2010.12.075

[5] E. Zeller, H. Beruda, and H. Schmidbaur, “Tetrahedral gold cluster [Au$_4^{2+}$]: crystal structure of [[(tert-Bu)$_3$PAu]$_4^{2+}$]$_2$(BF$_4$)$_2$•2CHCl$_3$, Inorg. Chem., vol. 32, no. 15, pp. 3203-3204, 1993, doi: 10.1021/ic00067a002.

[6] C. E. Briant, K. P. Hall, D. M. P. Mingos and A. C. Wheeler, “Synthesis and structural characterisation of hexakis(triphenyl phosphine)hexagold(2+) nitrate, [Au$_6$(PPh$_3$)$_6$][NO$_3$]$_2$, and related clusters with edgesharing bitetrahedral geometries”, J. Chem. Soc., Dalton Trans., No. 3, pp. 687-692, 1986, doi: 10.1039/DT9860000687.

[7] K. Konishi, “Phosphine-coordinated pure-gold clusters: Diverse geometrical structures and unique optical properties/responses,” Structure and Bonding, vol. 161. Springer Verlag, pp. 49–86, 10-Apr- 2014.

[8] Y. Shichibu, M. Zhang, Y. Kamei, and K. Konishi, “[Au$_7^{3+}$]: A missing link in the four-electron gold cluster family,” J. Am. Chem. Soc., vol. 136, no. 37, pp. 12892–12895, 2014. doi: 10.1021/ja508005x.

[9] B. S. Gutrath, U. Englert, Y. Wang, U. Simon, “Molecular and Electronic Structure of the Cluster [Au$_6$(PPh$_3$)$_6$](NO$_3$)$_2$, Eur. J. Inorg. Chem., vol. 2016, no. 7, pp. 975–981, Mar. 2016. doi: 10.1002/ejic.201300148.

[10] R. Sekine, A. Murono, M. Okakura, Y. Kobayashi, Y. Nakagami, “Analysis for the stability of all sodium isomers by graph theory and molecular mechanics”, J. Comput. Chem. Jpn., vol. 17, no. 3, pp. 117-119, 2018, doi: 10.2477/jccj.2018-0026. (in japanese)

[11] R. Sekine, A. Murono, Y. Kobayashim and Y. Nakagami, “Graph theoretical study on metal clusters (4)”, Bull. Soc. DV-Xα, vol. 31, pp.103-106, 2018. (in japanese)

[12] J. I. Aihara, “Graph theory of aromatic stabilization,” Bulletin of the Chemical Society of Japan, vol. 89, no. 12., pp. 1425–1454, 2016

[13] S. Plimpton, A. Thompson, S. Moore, A. Kohlmeyer, and R. Berger, “LAMMPS Molecular Dynamics Simulator”, https://lammps.sandia.gov/.

[14] R. Sekine, M. Okakura, and Y. Nakagami, “Screening of achievable Na clusters by molecular mechanics method”, Bull. Soc. DV-Xα, vol. 31, pp. 107-110, 2018. (in japanese)

[15] T. Tsukuda, “Structures of chemically modified superatoms toward creation of artificial atoms and quasi-molecules in nanoscale”, Mol. Sci., vol. 13, A0108, 2019. doi: 10.3175/molsci.13.A0108. (in japanese).