Articles

Toward an Accurate Self-interaction Binding Energy of Magic Cluster TiAu₄

Young-Kyu Han, Jong Chan Kim, Jaehoon Jung, and Ungsik Yu[†,*]

Computational Chemistry Laboratory, Corporate R&D, LG Chem, Ltd. Research Park, Daejeon 305-380, Korea
*†Gachon University of Medicine and Science, Incheon 406-840, Korea. *E-mail: ungsik@gachon.ac.kr*

We performed coupled-cluster calculations to determine the intermolecular interaction energy between two TiAu₄ clusters. Our ab initio calculations predict that the binding energy is 2.89 eV, which is somewhat larger than the known binding energy of 2.0 eV for TiH₄-TiH₄. The intermolecular binding energy is relatively high, despite TiAu₄ having all the attributes of a magic cluster. The favorable orbital interaction between occupied Au(6s) and unoccupied Ti(3d) orbitals leads to the strong dimeric interaction for TiAu₄-TiAu₄.

Key Words : TiAu₄, Binding energy, Dimeric interaction

Introduction

Magic clusters are characterized by low electron affinity, high ionization potential and enhanced stability. Their unwillingness to either accept or donate an electron makes them relatively inert, and two magic clusters would be expected to interact weakly *via* a van der Waals-like mechanism.[1,2] For magic cluster, the presence of closed electronic shells alone may not be a sufficient criterion for determining its suitability as a building block of cluster-assembled materials.[3] Thus, the investigation of dimer formation of magic clusters is important in the context of novel materials.[4] Ghanty et al.[5] using ab initio calculations showed that (TiAu₄)₂ has very strong dimeric interaction, although TiAu₄ has all the attributes of a magic cluster, *i.e.*, ionization potential of 9.73 eV, electron affinity of 0.63 eV, and HOMO-LUMO gap of 3.24 eV. The Becke three parameter Lee-Yang-Parr (B3LYP)[6,7] and Moller-Plesset second-order perturbation theory (MP2)[8] methods were employed in that study. Ghanty and co-workers[5] concluded from their MP2 calculations that the interaction energy of 7.04 eV between the magic clusters is unusually large, although the B3LYP interaction energy is only 2.16 eV. However, Han[9] demonstrated that the MP2 interactions are exaggerated due to neglection of the basis set superposition error (BSSE).

We note that the B3LYP (1.88 eV) and MP2 (4.63 eV) results[9] are still different even the values are stabilization energies taking into consideration BSSE and fragment relaxation. This dimeric system may be a real challenge for quantum chemistry, as the ten transition-metal atoms introduce large amounts of dynamic correlation, that are not well described by low-level wavefunction methods such as MP2.[10] In the present study, we recalculated the interaction energies between the clusters using the theory of high-level coupled-cluster levels, *i.e.*, coupled-cluster singles, doubles, and perturbative triples [CCSD(T)].[11]

Computation Details

A large basis CCSD(T) calculation on a species with ten transition metal atoms is too difficult to perform except with small basis sets. To solve this problem, we employed an "additive" approach, which rests on the fact that higher-order electron correlation effects tend to be very insensitive to improvements in the basis.[12-14]

CCSD(T) est/large BasisII
= CCSD(T)/BasisI + [MP2/BasisII − MP2/BasisI]

The stabilization energy (ΔE)[15-17] was obtained as

$$\Delta E = E_{AB}^{\alpha \cup \beta}(AB) - E_{AB}^{\alpha \cup \beta}(A) - E_{AB}^{\alpha \cup \beta}(B) + E_{rel}^{\alpha}(A) + E_{rel}^{\beta}(B)$$

where $E_{rel}^{\alpha}(A) = E_{AB}^{\alpha}(A) - E_A^{\alpha}(A)$ and $E_{rel}^{\beta}(B) = E_{AB}^{\beta}(B) - E_B^{\beta}(B)$ are the fragmentation relaxation energies that correspond to the energy penalty for distorting from their isolated geometries to the geometries of the complex. In the formula, the electronic energy of a molecular system M, at geometry G, computed with basis set σ is defined as $E_G^{\sigma}(M)$. We used three different size of basis sets: Basis1 - (8s7p6d1f)/[6s5p3d1f] for Ti[18] and (8s7p6d)/[6s5p3d] for Au.[19] Basis2 - (8s7p6d1f)/[6s5p3d1f] for Ti[18] and (8s7p6d2f)/[6s5p3d2f] for Au.[19] and Basis3 - all-electron (21s16p9d3f2g)/[7s8p6d3f2g] for Ti[20,21] and (8s7p6d3f2g)/[6s5p3d3f2g] for Au.[19] The number of valence electrons is 12 for Ti and 19 for Au in the relativistic effective core potential (RECP) calculations.[18,19] Stationary points were characterized as local minima by calculating the energy second derivatives. All the calculations were performed with the Gaussian03 package.[22] All occupied and virtual orbitals were included at all levels of the theory.

Results and Discussion

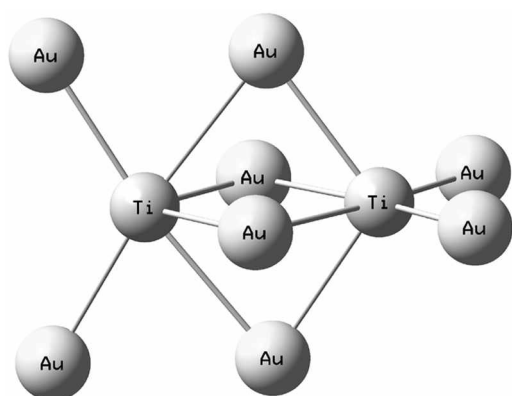The optimized structure (TiAu₄)₂ is shown in Figure 1.

Figure 1. D_{2d} Optimized structures of Ti$_2$Au$_8$.

The gross geometrical features of the individual clusters are retained in the dimer.[5] The stabilization energies computed at the density functional theory (DFT) and ab initio levels of theory are summarized in Table 1. The effectiveness of the basis set extension is quite different in wavefunction-based theories and density-based theories. The convergence with respect to the basis set size is much faster with the density-based methods than with the post-Hartree-Fock methods such as MP2. This has already been found before in other comparative studies.[23-25] It follows from the fact in the DFT approach the orbitals are only needed to construct the density.

For practical reason, the coupled-cluster calculations were performed with Basis1. It is worth noting that the CCSD(T) energy of 1.66 eV is much less than the MP2 energy of 4.01 eV, indicating that the MP2 value is overestimated for the system. It is well known that local density approximation (LDA) suffers from a problem of overbinding.[26] We tested a LDA functional, Slater exchange and Vosko-Wilk-Nusair correlation (SVWN),[27,28] for TiAu$_4$-TiAu$_4$ (see Table 1) and obtained 4.43-4.61 eV, comparable to the MP2 values and supporting the overestimation of MP2 method for the system. The extension of basis sets increases the stabilization energies at the MP2 level, and the estimated CCSD(T)/Basis3 value is 2.89 eV. The intermolecular binding energy is relatively high, despite TiAu$_4$ having all the attributes of a magic cluster.[5] As shown in Table 1, the Perdew-Wang91 (PW91)[29] results are in good agreement with the CCSD(T) est value, while the B3LYP values are very underestimated.

Since gold can behave like hydrogen,[30] we compared the binding energies of (TiAu$_4$)$_2$ with that of (TiH$_4$)$_2$. The most

Table 1. The stabilization energies (in eV) computed at the SVWN, PW91, B3LYP, MP2, CCSD, and CCSD(T) levels of theory for TiAu$_4$-TiAu$_4$. The values in italic are estimated values (see text)

	SVWN[a]	PW91[a]	B3LYP[a]	MP2	CCSD[b]	CCSD(T)[b]
Basis1	4.46	2.84	2.07	4.01	1.18	1.66
Basis2	4.61	2.88	2.05	4.65	1.82	2.30
Basis3	4.43	2.72	1.88	5.24	2.41	*2.89*

[a]The interaction energies without BSSE correction. The BSSE is small in the DFT calculations. See Reference 9. [b]The MP2 optimized geometries were used.
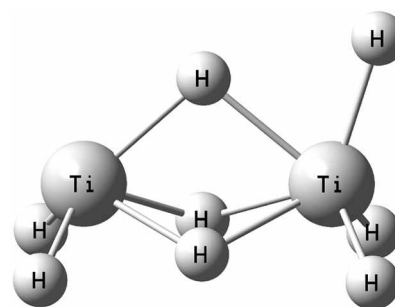

Figure 2. C_s Optimized structures of Ti$_2$H$_8$.

Table 2. The interactrion energies (in eV) computed at the SVWN, PW91, and B3LYP levels of theory for TiH$_4$-TiH$_4$

	SVWN	PW91	B3LYP	MP2[a]	CCSD(T)[a]
Binding energy	3.28	2.16	1.49	2.03	2.00

[a]The MP2 optimized geometries were used. The TZVP and TZVP(f) basis sets were employed for the MP2 and CCSD(T) calculations, respectively. Reference 31.

stable form is H$_2$Ti(μ-H)$_3$TiH$_3$, as depicted in Figure 2.[31] The SVWN, PW91, and B3LYP binding energies for (TiH$_4$)$_2$ are listed in Table 2, along with the reported MP2 and CCSD(T)// MP2 results.[31] The basis sets ($8s7p6d1f$)/[$6s5p3d1f$] for Ti[30] and ($4s1p$)/[$2s1p$] for H[32] were used. The TiAu$_4$-TiAu$_4$ binding energy is 0.89 eV larger than that for TiH$_4$-TiH$_4$ (2.00 eV). Similarly to the case of (TiAu$_4$)$_2$, the PW91 result agrees considerably better with the CCSD(T) value for (TiH$_4$)$_2$, while the B3LYP value is underestimated. For Au$_2$, the PW91 functional provides a Au-Au binding energy (2.28 eV) for Au$_2$ close to the experimental data[23] of 2.31 eV, whereas the B3LYP functional gives a much smaller value (1.93 eV). These results show that PW91 is a practical and efficient method of choice for determining the binding energies of similar systems.

Let us now examine the origin of the strong dimeric interaction for TiAu$_4$. In Table 3, the results of the fragment-based energy decomposition[34] of the dimeric interaction are presented for TiAu$_4$-TiAu$_4$ and TiH$_4$-TiH$_4$. The DFT calculations on the binding energies have been performed with the

Table 3. Energy decomposition (in eV) for the TiAu$_4$-TiAu$_4$ and TiH$_4$-TiH$_4$ binding energies

	(TiAu$_4$)$_2$	(TiH$_4$)$_2$
ΔE	−2.80	−2.25
ΔE_{def}	+0.70	+1.09
ΔE_{steric}	+5.87	+1.95
ΔE_{pauli}	+22.99	+7.77
ΔE_{elast}	−17.12	−5.82
ΔE_{oi}	−9.37	−5.29
	A1 −4.13	
	A2 −0.50	
	B1 −2.37[a]	
	B2 −2.37[a]	

[a]The degenerated B1 and B2 values correspond to the polarization orbital interaction.

24A1
65.3 % Au $6s$
11.4 % Ti $3d_{x^2-y^2}$

26A1
61.6 % Ti $3d_{x^2-y^2}$
15.6 % Au $6s$

18B1
67.4 % Au $6s$
9.4 % Ti $3d_{xz}$
8.8 % Au $5d_{xz}$

19B1
65.5 % Ti $3d_{xz}$
12.4 % Au $6s$

18B2
65.5 % Au $6s$
12.0 % Au $5d_{yz}$
11.0 % Ti $3d_{yz}$
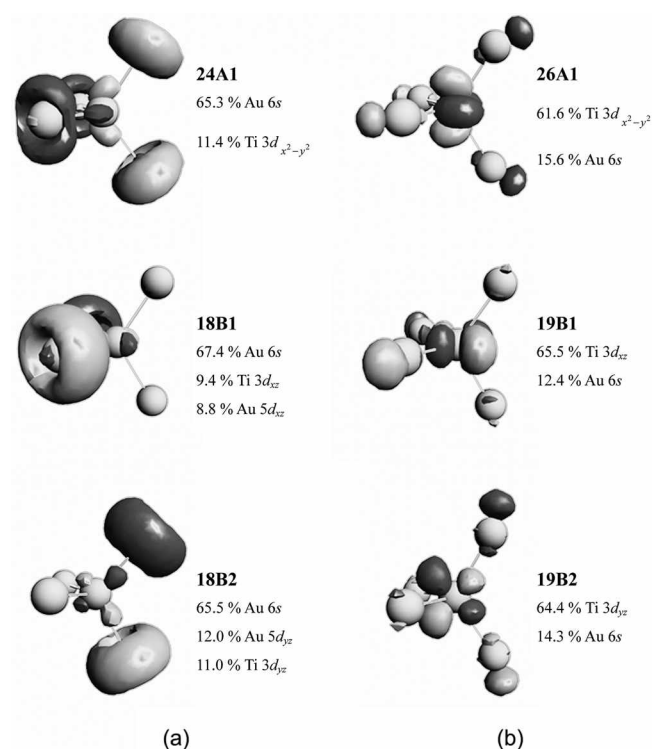
19B2
64.4 % Ti $3d_{yz}$
14.3 % Au $6s$

(a)   (b)

Figure 3. Main occupied-unoccupied contributions of the irreducible representations to the stabilizing orbital-interaction energy for TiAu₄-TiAu₄: (a) occupied orbitals and (b) unoccupied orbitals.

ADF2005 package.[35] This program allows us to consider relativistic effects by means of the zero order regular approximation (ZORA) approach. The bond energy can be decomposed into contributions from three terms:

$$\Delta E = \Delta E_{def} + \Delta E_{steric} + \Delta E_{oi}$$

The deformation energy (ΔE_{def}) is the energy necessary to deform the bonding moieties from their respective isolated equilibrium geometries into the geometries they assume in the bound complex. The steric energy (ΔE_{steric}) is the sum of two terms, one corresponding to the electrostatic interaction (ΔE_{elst}) between the fragments and the other to the Pauli repulsion energy (ΔE_{pauli}). ΔE_{steric} should not be confused with the loosely defined steric interaction between substituents in a molecule. The orbital interaction energy (ΔE_{oi}) is the energy due to the attractive interactions between occupied orbitals of one fragment and empty orbitals of the other fragment, as well as between the occupied and empty orbitals within a given fragment (polarization). ΔE_{oi} can be decomposed into orbital contributions from each irreducible representation of the interacting system. The steric term is usually repulsive at the equilibrium distance because the repulsive component ΔE_{pauli} dominates, such as in this work, and it is more repulsive for the TiAu₄-TiAu₄ interaction than for TiH₄-TiH₄. The favorable interaction mainly originates from the orbital interaction between occupied Au($6s$) and unoccupied Ti($3d_{x^2-y^2}$, $3d_{xz}$, $3d_{yz}$) orbitals, as shown in Figure 3. The $5d$ orbital contribution of Au is found to be minor.

Conclusions

We performed coupled-cluster calculations to determine the intermolecular interaction energy between two TiAu₄ clusters. Our ab initio calculations predict that the binding energy is 2.89 eV, which is somewhat larger than the known binding energy of 2.0 eV for TiH₄-TiH₄. PW91 is a practical and efficient method of choice for determining the binding energies of similar systems. The intermolecular binding energy is relatively high, despite TiAu₄ having all the attributes of a magic cluster. Energy decomposition analysis shows that the favorable orbital interaction between occupied Au($6s$) and unoccupied Ti($3d$) orbitals leads to the strong dimeric interaction for TiAu₄-TiAu₄.

References

1. Saito, S.; Ohnishi, S. *Phys. Rev. Lett.* **1987**, *59*, 190.
2. Khanna, S. N.; Jena, P. *Phys. Rev. Lett.* **1992**, *69*, 1664.
3. Hakkinen, H.; Manninen, M. *Phys. Rev. Lett.* **1996**, *76*, 1599.
4. Nigam, S.; Majumder, C.; Kulshreshtha, S. K. *Phys. Rev. B* **2006**, *73*, 115424.
5. Ghanty, T. K.; Chandrakumar, K. R. S.; Ghosh, S. K. *J. Chem. Phys.* **2004**, *120*, 11363.
6. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
7. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
8. Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275.
9. Han, Y.-K. *J. Chem. Phys.* **2005**, *122*, 136101.
10. Pyykko, P. *Inorg. Chim. Acta* **2005**, *358*, 4113.
11. Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513.
12. Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M. *J. Chem. Phys.* **2004**, *120*, 647.
13. Han, Y.-K. *J. Chem. Phys.* **2006**, *124*, 24316.
14. Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2006**, *110*, 10656.
15. Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
16. Mayer, I.; Surjan, P. R. *Chem. Phys. Lett.* **1992**, *191*, 497.
17. Xantheas, S. S. *J. Chem. Phys.* **1996**, *104*, 882.
18. Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866.
19. Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
20. Bauschlicher, Jr., C. W. *Theor. Chem. Acc.* **1999**, *103*, 141.
21. Bauschlicher, Jr., C. W. *Theor. Chim. Acta* **1995**, *92*, 183.
22. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*; Gaussian Inc.: Wallingford, CT, 2004.

308   *Bull. Korean Chem. Soc.* **2008**, Vol. 29, No. 2

Young-Kyu Han et al.

23. Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1992**, *197*, 499.
24. Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1994**, *231*, 345.
25. Hertwig, R. H.; Koch, W. *J. Comput. Chem.* **1995**, *16*, 576.
26. Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.
27. Slater, J. C. *Quantum Theory of Molecular and Solids. Vol. 4: The Self-Consistent Field for Molecular and Solids*; McGraw-Hill: New York, 1974.
28. Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
29. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

30. Pyykkö, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 4412, the references are therein.
31. Webb, S. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 7195.
32. Dunning, Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
33. Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, vol. IV, Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.
34. Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.
35. Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.