Inorg. Chem. **2002**, *41*, 6332–6342

Inorganic Chemistry
Article

Assessment of Relative Stabilities of Positional Isomers of Polyhedral Heteronuclear Clusters via a Simplified Method of Bond Energy Calculations Based on Tight-Binding Approach and Adjacent Matrix Method: Applications to Binary Icosahedral Clusters

Boon K. Teo* and Alex Strizhev[†]

University of Illinois at Chicago, Department of Chemistry, 845 West Taylor Avenue, Room 4500, Chicago, Illinois 60607

Received May 7, 2002

A new and simple method for assessing the relative stabilities of various positional isomers of a given heteronuclear cluster is described. The method is based on a tight-binding approach in conjunction with an adjacent matrix methodology (TBAM). The usefulness of the method is illustrated by bond energy calculations of a number of binary icosahedral clusters, including noncentered icosahedral A_nB_{12-n} clusters comprising main-group elements B, C, N, and S as well as B- and A-centered icosahedral A_nB_{13-n} clusters that consist of transition metals, Au, Ag, Ni, and Pt atoms. The latter results are compared with the previously reported molecular mechanics calculations based on Lennard-Jones potential and with experimental results, whenever possible. The trends of the total bond energies obtained by the two methods are nearly parallel in all cases, indicating that the relative stabilities predicted by the two methods follow the same order. The TBAM approach provides a simple and efficient way of predicting the relative stabilities of various positional isomers of a given cluster, particularly for clusters where the number of positional isomers is so large that it cannot be handled manually. The total bond energies exhibit a stepwise progression. Each step is characterized by a set of A–A, B–B, and A–B bonds which uniquely determines the total bond energy and, hence, the stability. The step formation implies that positional isomers of a given cluster geometry can be categorized by sets of numbers of A–A, B–B, and A–B bonds, or simply the numbers of the minority (either A–A or B–B) bonds. Three site preference rules, the strong-bond rule, the heterobond rule, and the big-hole rule, were formulated based on these model calculations. These rules are useful in rationalizing and/or predicting the relative stabilities of various positional isomers of a given cluster geometry.

Introduction

The determination of the relative stabilities of various positional isomers[1] of a given polyhedral heteronuclear cluster composed of different kinds of atoms is a matter of significant importance in such diverse fields as alloy formation, site preference of molecular clusters and intermetallic phases, and reactivities and selectivities of multimetallic catalysts, as well as in the transition from molecular to bulk behavior.[2−17] One way to assess the stabilities of various positional isomers of multicolored clusters is to calculate the

---

* To whom correspondence should be addressed. E-mail: boonkteo@uic.edu.

[†] Present address: Tripos, Inc., 1699 South Hanley Rd., Suite 303, St. Louis, MO 63144.

(1) The word "stereoisomer" was used in our previous publications in the broader sense of stereochemically nonsuperimposable structures. Strictly speaking, stereoisomers have the same atom-to-atom connections but different, nonsuperimposable shapes (i.e., different arrangements in space). Hence, the different "structural isomers" (with different atom-to-atom connectivities) studied here are best considered as "positional isomers" or "constitutional isomers". In this sense, "positional isomers" are structural isomers with the same set of atoms occupying different positions of a polyhedral framework.

(2) (a) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383. (b) Deng, H. T.; Kerns, K. P.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 446.

(3) *Physics and Chemistry of Metal Cluster Compounds: Model Systems for Small Metal Particles*; de Jongh, L. J., Ed.; Kluwer Academic: Boston, 1994.

(4) Micklitz, W.; McKee, V.; Rardin, R. L.; Pence, L. E.; Papaefthymiou, G. C.; Bott, S. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 8061.

(5) *Clusters and Colloids: From Theory to Applications*; Schmid, G., Ed.; VCH: Weinheim, 1994.

(6) Zheng, Z.; Knobler, C. B.; Mortimer, M. D.; Kong, G.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 1235.

(7) Shore, S. G. *Pure Appl. Chem.* **1994**, *66*, 263.

(8) *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990.

10.1021/ic020325b CCC: $22.00

"total bond energies" of the clusters. Recently, we reported molecular mechanics calculations of mixed-metal icosahedral clusters that consist of two kinds of atoms, A and B, as exemplified by the Ag−Au, Pt−Au, and Ni−Au systems, using the Lennard-Jones (L-J) potential (ref 18). In this study (hereafter referred to as the L-J method), the atoms were allowed to move in the minimization of the total bond energies of the clusters. Hence, we obtained not only the relative stabilities of the various positional isomers of a given composition of the heteronuclear cluster based on the calculated total bond energies but also the optimized structure.[18] However, our previous work[18] indicated that the shifts in the atomic positions of the energy-minimized clusters, as compared with the starting geometries constructed with standard bond lengths, are, in general, rather small.

The previously mentioned calculations were performed for centered icosahedral binary clusters (with two kinds of atoms). If we increase the number of kinds of atoms (say to three for ternary clusters) or consider a larger cluster such as a pentagonal dodecahedron, the number of possible configurations increases dramatically, and it becomes increasingly difficult to account for all the positional isomers in order to assess their relative stabilities. For example, a binary pentagonal dodecahedron has 17824 configurations[19] as predicted by the Polya theorem.[20,21] It is impossible to manually calculate (or, more precisely, minimize) the energies of all the configurations of such a system. One solution to this problem is to fix the positions of the atoms in the cluster (at the standard bond lengths) and calculate the binding energies of the clusters based solely on the number of bonds between neighboring atoms: the tight-binding (TB) approach. By not allowing the atoms to move ("frozen" clusters, i.e., clusters with fixed atomic positions) and by focusing on only nearest-neighbor interactions, the computation time for each configuration can be greatly reduced. If we further assume that the bond energy for each type of bond does not vary significantly from the standard values (as indicated by our recent work[18]), the energy calculation (or, more precisely, minimization) based on the Lennard-Jones potential as detailed in ref 18 can be bypassed completely. In this case, the total binding energy of a particular positional isomer can be obtained by summing up the contributions from each type of bond within the cluster which in turn can be obtained by multiplying the numbers of bonds of each type by the corresponding bond energies. This gives rise to a simple method of assessing the relative stabilities of various positional isomers of heteronuclear clusters which is the goal of this paper.

The application of this tight-binding approach to heteronuclear clusters of increasing complexity and nuclearity relies on our ability to count the numbers of nearest-neighbor bonds of each type. It turns out the nearest-neighbor interactions can be described by the adjacent matrices (AM), which are already encrypted in the computer algorithm we developed for heteronuclear clusters with various cluster geometries including, for example, icosahedral geometry.[22] By combining the tight-binding approach with the adjacent matrix (TBAM), we have developed a new and efficient method for the calculation of bond energies of various positional isomers of heteronuclear clusters of increasing complexity and nuclearity such as the icosahedron and pentagonal dodecahedron. This paper describes the TBAM method and reports the results of such bond energy calculations on a number of binary icosahedral clusters, as exemplified by the mixed main-group C−B, N−B, and S−B systems as well as the mixed transition-metal Ag−Au, Pt−Au, and Ni−Au systems. These latter systems were chosen so that the results can be compared with the previously reported results based on molecular mechanics calculations using L-J potentials (ref 18). The usefulness of this tight-binding approach based on the adjacent matrix (TBAM) method is evident from the fact that it eliminates the time-consuming task of energy minimization or the L-J calculations of a large number of configurations. It requires, instead, only the relative energies of A−A and B−B bonds, the relative electronegativities of A and B, and the numbers of A−A, B−B, and A−B bonds for, say, a binary system. It is particularly useful in cases where the number of positional isomers is very large; for example, the previously mentioned binary pentagonal dodecahedron[19] has a large number of configurations which cannot be handled manually. Needless to say, for smaller clusters, more sophisticated theoretical approaches to the problem such as molecular orbital calculations are methods of choice.[23−26]

Nomenclature and the Numbering System

The nomenclature and the numbering system for heteronuclear cluster configurations are described in ref 18. We shall use this numbering system, which is consistent with

---

(9) Lipscomb, W. N. *Boron Hydrides*; W. A. Benjamin, Inc.: New York, 1963.

(10) (a) Grimes, R. N. *Coord. Chem. Rev.* **1995**, *143*, 71. (b) Grimes, R. N. *Carboranes*; Academic: New York, 1970.

(11) Coucouvanis, D.; Kanodia, S.; Swenson, D.; Chen, S. J.; Stuedemann, T.; Baenziger, N. C.; Pedelty, R.; Chu, M. *J. Am. Chem. Soc.* **1993**, *115*, 11271.

(12) Fenske, D.; Holstein, W. *Angew. Chem.* **1994**, *106*, 1311.

(13) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1993**, *115*, 11165.

(14) (a) Aur, S.; Kofalt, D.; Waseda, Y.; Egami, T.; Chen, H. S.; Teo, B. K.; Wang, R. *J. Non-Cryst. Solids* **1984**, *61−62*, 331. (b) Aur, S.; Kofalt, D.; Waseda, Y.; Egami, T.; Wang, R.; Chen, H. S.; Teo, B. K. *Solid State Commun.* **1983**, *48*, 111.

(15) (a) Rieck, D. F.; Montag, R. A.; McKechnie, T. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 1330. (b) Kahaian, A. J.; Thoden, J. B.; Dahl, L. F. *J. Chem. Soc., Chem. Commun.* **1992**, 353.

(16) (a) Albano, V. G.; Demartin, F.; Iapalucci, M. C.; Longoni, G.; Sironi, A.; Monan, M.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1992**, 497. (b) Albano, V. G.; Demartin, F.; Iapalucci, M. C.; Longoni, G.; Monan, M.; Zanello, P. Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993**, 173.

(17) (a) Teo, B. K.; Zhang, H. *Coord. Chem. Rev.* **1995**, *143*, 609. (b) Zhang, H.; Teo, B. K. *Inorg. Chim. Acta*. **1997**, *265*, 213. (c) Teo, B. K.; Dang, H. Campana, C.; Zhang, H. *Polyhedron* **1998**, *17*, 617. (d) Zhang, H.; Teo, B. K. *Inorg. Chim. Acta*. **2001**, *317*, 1−11.

(18) Teo, B. K.; Strizhev, A.; Elber, R.; Zhang, H. *Inorg. Chem.* **1998**, *37*, 2482.

(19) Teo, B. K.; Strizhev, A. To be published.

(20) Polya, G. *Acta Math.* **1937**, *68*, 145.

(21) Teo, B. K.; Zhang, H.; Kean, Y.; Dang, H.; Shi, X. *J. Chem. Phys.* **1993**, *99*, 2929.

(22) Teo, B. K.; Strizhev, A. *J. Cluster Sci*. **2002**, *13*, 247−261.

(23) Gimarc, B. M.; Zhao, M. *Inorg. Chem*. **1996**, *35*, 825−834.

(24) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem*. **1998**, *37*, 3454−3470.

(25) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489.

(26) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc*. **1977**, *99*, 7834.

the IUPAC nomenclature, throughout this paper. Specifically, to avoid ambiguities in naming positional isomers, we adopt two simple rules:[18] (1) the "lowest possible consecutive indices" are chosen for the minority atoms, and (2) each consecutive index must be greater than the one preceding it. For example, 1,7,9-A_3B_{10} represents a B-centered icosahedral cluster with three minority A atoms at positions 1, 7, and 9. Because the minority A atoms are "isolated" (i.e., separated by the majority B atoms) in this cluster, it can be classified as a three-fragment cluster.

Adjacent Matrix Method

The symmetry-based algorithm used to generate, in a systematic fashion, all possible positional isomers of a heteronuclear polyhedral cluster had been described in detail in ref 22. It utilizes two arrays: array1 and array2. Array1-(i,j) is a two-dimensional array where the first dimension i corresponds to the number of the current configuration and the second dimension j corresponds to the designator (current number) of the minority atom in the cluster. The value of array1 is the IUPAC position index of the minority atom. Array1 represents the minority configurations in the way described previously. For computational purposes, we need to generate a second two-dimensional array, array2(i,k). Here, the first dimension i represents also the number of the current configuration while the second dimension k runs through all the positions in the cluster. The values of array2 can only be "0" or "1" where "1" represents the presence of a minority atom at the position and "0" represents the presence of the majority atom at the position. As an example, let us describe the configuration 1,2,4,11-A_4B_9 of an icosahedral cluster which is the 10th configuration (current number). Then, array1 will look like array1(10,1) = 1; array1(10,2) = 2; array1(10,3) = 4; array1(10,4) = 11.

Here, the first number in the parentheses in array1 is the current configuration number (10), while the second number is the number of the atom of the second kind (minority atoms). Because we have 4 minority atoms in this example, the maximum number in the second dimension is 4.

At the same time, array2 will look like array2(10,1) = 1; array2(10,2) = 1; array2(10,3) = 0; array2(10,4) = 1; array2-(10,5) = 0; array2(10,6) = 0; array2(10,7) = 0; array2(10,8) = 0; array2(10,9) = 0; array2(10,10) = 0; array2(10,11) = 1; array2(10,12) = 0; array2(10,13) = 0.

As can be seen, the first number in the parentheses in array2 is the current configuration number (10), while the second number is the position of the minority atom in the cluster. The value of array2(i,k), 1 or 0, signifies the presence (1) or the absence (0) of a minority atom at the kth position. In this example, positions 1,2,4,11 are occupied by minority atoms. Furthermore, the maximum number in the second dimension for an icosahedron is 13 because a centered icosahedron has 13 positions.

Given these arrays, all the configurations can be tracked and the numbers of A−A, A−B, and B−B bonds can be easily determined. For the previous example, values of array2(10,1) = 1 and array2(10,2) = 1 mean that there is an A−A bond between atoms in positions 1 and 2; values of array2(10,2) = 1 and array2(10,3) = 0 mean that there is a A−B bond between atoms in the positions 2 and 3; finally, values of array2(10,5) = 0 and array2(10,6) = 0 mean that there is a B−B bond between atoms in the positions 5 and 6.

Table 1. Adjacent Matrix for 1,2-A_2B_{11} Positional Isomers[a]

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	0	1	3	3	3	3	0	0	0	0	0	0	3
2	1	0	3	0	0	3	3	0	0	0	2	0	3
3	3	3	0	2	0	0	2	2	0	0	0	0	2
4	3	0	2	0	2	0	0	2	2	0	0	0	2
5	3	0	0	2	0	2	0	0	2	2	0	0	2
6	3	3	0	0	2	0	0	0	0	2	2	0	2
7	0	3	2	0	0	0	0	2	0	0	2	2	2
8	0	0	2	2	0	0	2	0	2	0	0	2	2
9	0	0	0	2	2	0	0	2	0	2	0	2	2
10	0	0	0	0	2	2	0	0	2	0	2	2	2
11	0	2	0	0	0	2	2	0	0	2	0	2	2
12	0	0	0	0	0	0	2	2	2	2	2	0	2
13	3	3	2	2	2	2	2	2	2	2	2	2	0

[a] Value 0 denotes the absence of a bond between atoms, value 1 designates the AA bond between two A atoms, value 2 denotes the BB bond between two B atoms, and value 3 represents the AB bond between an A atom and a B atom.

Now we can make use of array2 in the construction of the adjacent matrix. An example is given in Table 1 for the 1,2-A_2B_{11} positional isomer of a centered icosahedron. The adjacent matrix is a diagonal matrix and has dimensions of 13 × 13 with the row and the column representing atomic positions. The matrix elements indicate the types of bonds between the atoms. Value "0" denotes the absence of a bond between the corresponding positions, value "1" denotes an A−A bond between the atoms occupying the corresponding positions, value "2" denotes a B−B bond between the atoms, and finally, value "3" denotes an A−B bond between the atoms. Now, to calculate numbers of bonds of three kinds, N_{AA}, N_{BB}, and N_{AB}, one needs only to calculate the number of 1s, 2s, and 3s accordingly. So, given the adjacent matrices, the numbers of A−A, B−B, and A−B bonds for each configuration can easily be calculated. Results are presented here for noncentered A_nB_{12-n} icosahedral clusters (Table 2), as well as B-centered (Table 3) and A-centered (Table 4) A_nB_{13-n} icosahedral clusters.

It should be emphasized that the computational details discussed in this section are for the sole purpose of illustrating how the numbers of different types of bonds can be derived from the adjacent matrices. The latter are encrypted in the symmetry-based algorithm used to generate the positional isomers. To apply the TBAM method, however, one needs only the numbers of A−A, B−B, and A−B bonds such as those tabulated in Tables 2−4 for a binary icosahedral cluster system.

Bond Energy Calculations

Given the knowledge of the number of bonds of each kind and the assumption that only the nearest neighbor interactions (i.e., the bonds) contribute to the cluster's total energy (in the spirit of the tight-binding approach), the "total bond energy" of a cluster can be calculated by summing up the

Table 2. Numbers of AA (N_{AA}), BB (N_{BB}), and AB (N_{AB}) Bonds for Noncentered Binary Icosahedral A_nB_{12-n} Clusters

noncentered icosahedral cluster	N_{AA}	N_{BB}	N_{AB}	noncentered icosahedral cluster	N_{AA}	N_{BB}	N_{AB}
B_{12}	0	30	0	1,2,3,4,10,12-A_6B_6	6	6	18
1-AB_{11}	0	25	5	1,2,3,5,8,10-A_6B_6	6	6	18
1,2-A_2B_{10}	1	21	8	1,2,3,5,8,11-A_6B_6	6	6	18
1,7-A_2B_{10}	0	20	10	1,2,3,5,8,12-A_6B_6	6	6	18
1,12-A_2B_{10}	0	20	10	1,2,3,5,9,12-A_6B_6	6	6	18
1,2,3-A_3B_9	3	18	9	1,2,3,5,10,12-A_6B_6	6	6	18
1,2,4-A_3B_9	2	17	11	1,2,3,9,10,12-A_6B_6	6	6	18
1,2,8-A_3B_9	1	16	13	1,2,4,7,9,12-A_6B_6	6	6	18
1,2,9-A_3B_9	1	16	13	1,2,4,9,11,12-A_6B_6	6	6	18
1,7,9-A_3B_9	0	15	15	1,2,4,7,8,10-A_6B_6	5	5	20
1,2,3,4-A_4B_8	5	15	10	1,2,4,7,9,10-A_6B_6	5	5	20
1,2,3,5-A_4B_8	4	14	12	1,2,4,7,10,12-A_6B_6	5	5	20
1,2,3,9-A_4B_8	3	13	14	1,2,3,4,5-B_5A_7	12	7	11
1,2,4,7-A_4B_8	3	13	14	1,2,3,4,9-B_5A_7	11	6	13
1,2,4,9-A_4B_8	3	13	14	1,2,3,4,10-B_5A_7	10	5	15
1,2,4,11-A_4B_8	3	13	14	1,2,3,5,8-B_5A_7	10	5	15
1,2,4,10-A_4B_8	2	12	16	1,2,3,5,9-B_5A_7	10	5	15
1,2,4,12-A_4B_8	2	12	16	1,2,3,5,10-B_5A_7	10	5	15
1,2,8,9-A_4B_8	2	12	16	1,2,4,7,8-B_5A_7	10	5	15
1,2,8,12-A_4B_8	2	12	16	1,2,3,5,12-B_5A_7	9	4	17
1,2,9,12-A_4B_8	2	12	16	1,2,3,9,10-B_5A_7	9	4	17
1,2,8,10-A_4B_8	1	11	18	1,2,4,7,9-B_5A_7	9	4	17
1,2,3,4,5-A_5B_7	7	12	11	1,2,4,7,12-B_5A_7	9	4	17
1,2,3,4,9-A_5B_7	6	11	13	1,2,4,9,11-B_5A_7	9	4	17
1,2,3,4,10-A_5B_7	5	10	15	1,2,4,7,10-B_5A_7	8	3	19
1,2,3,5,8-A_5B_7	5	10	15	1,2,4,10,12-B_5A_7	8	3	19
1,2,3,5,9-A_5B_7	5	10	15	1,2,3,4-B_4A_8	15	5	10
1,2,3,5,10-A_5B_7	5	10	15	1,2,3,5-B_4A_8	14	4	12
1,2,4,7,8-A_5B_7	5	10	15	1,2,3,9-B_4A_8	13	3	14
1,2,3,5,12-A_5B_7	4	9	17	1,2,4,7-B_4A_8	13	3	14
1,2,3,9,10-A_5B_7	4	9	17	1,2,4,9-B_4A_8	13	3	14
1,2,4,7,9-A_5B_7	4	9	17	1,2,4,11-B_4A_8	13	3	14
1,2,4,7,12-A_5B_7	4	9	17	1,2,4,10-B_4A_8	12	2	16
1,2,4,9,11-A_5B_7	4	9	17	1,2,4,12-B_4A_8	12	2	16
1,2,4,7,10-A_5B_7	3	8	19	1,2,8,9-B_4A_8	12	2	16
1,2,4,10,12-A_5B_7	3	8	19	1,2,8,12-B_4A_8	12	2	16
1,2,3,4,5,6-A_6B_6	10	10	10	1,2,9,12-B_4A_8	12	2	16
1,2,3,4,5,7-A_6B_6	9	9	12	1,2,8,10-B_4A_8	11	1	18
1,2,3,4,5,8-A_6B_6	9	9	12	1,2,3-B_3A_9	18	3	9
1,2,3,4,5,9-A_6B_6	9	9	12	1,2,4-B_3A_9	17	2	11
1,2,3,4,5,10-A_6B_6	8	8	14	1,2,8-B_3A_9	16	1	13
1,2,3,4,5,11-A_6B_6	8	8	14	1,2,9-B_3A_9	16	1	13
1,2,3,4,5,12-A_6B_6	7	7	16	1,7,9-B_9A_9	15	0	15
1,2,3,4,9,10-A_6B_6	7	7	16	1,2-B_2A_{10}	21	1	8
1,2,3,4,9,11-A_6B_6	7	7	16	1,7-B_2A_{10}	20	0	10
1,2,3,4,9,12-A_6B_6	7	7	16	1,12-B_2A_{10}	20	0	10
1,2,3,5,8,9-A_6B_6	7	7	16	1-BA_{11}	25	0	5
1,2,3,5,9,10-A_6B_6	7	7	16	A_{12}	30	0	0

Table 3. Numbers of AA (N_{AA}), BB (N_{BB}), and AB (N_{AB}) Bonds for B-Centered Binary Icosahedral A_nB_{13-n} Clusters

B-centered icosahedral cluster	N_{AA}	N_{BB}	N_{AB}	B-centered icosahedral cluster	N_{AA}	N_{BB}	N_{AB}
B_{13}	0	42	0	1,2,3,4,10,12-A_6B_7	6	12	24
1-AB_{12}	0	36	6	1,2,3,5,8,10-A_6B_7	6	12	24
1,2-A_2B_{11}	1	31	10	1,2,3,5,8,11-A_6B_7	6	12	24
1,7-A_2B_{11}	0	30	12	1,2,3,5,8,12-A_6B_7	6	12	24
1,12-A_2B_{11}	0	30	12	1,2,3,5,9,12-A_6B_7	6	12	24
1,2,3-A_3B_{10}	3	27	12	1,2,3,5,10,12-A_6B_7	6	12	24
1,2,4-A_3B_{10}	2	26	14	1,2,3,9,10,12-A_6B_7	6	12	24
1,2,8-A_3B_{10}	1	25	16	1,2,4,7,9,12-A_6B_7	6	12	24
1,2,9-A_3B_{10}	1	25	16	1,2,4,9,11,12-A_6B_7	6	12	24
1,7,9-A_3B_{10}	0	24	18	1,2,4,7,8,10-A_6B_7	5	11	26
1,2,3,4-A_4B_9	5	23	14	1,2,4,7,9,10-A_6B_7	5	11	26
1,2,3,5-A_4B_9	4	22	16	1,2,4,7,10,12-A_6B_7	5	11	26
1,2,3,9-A_4B_9	3	21	18	1,2,3,4,5,13-B_6A_7	12	12	18
1,2,4,7-A_4B_9	3	21	18	1,2,3,4,9,13-B_6A_7	11	11	20
1,2,4,9-A_4B_9	3	21	18	1,2,3,4,10,13-B_6A_7	10	10	22
1,2,4,11-A_4B_9	3	21	18	1,2,3,5,8,13-B_6A_7	10	10	22
1,2,4,10-A_4B_9	2	20	20	1,2,3,5,9,13-B_6A_7	10	10	22
1,2,4,12-A_4B_9	2	20	20	1,2,3,5,10,13-B_6A_7	10	10	22
1,2,8,9-A_4B_9	2	20	20	1,2,4,7,8,13-B_6A_7	10	10	22
1,2,8,12-A_4B_9	2	20	20	1,2,3,5,12,13-B_6A_7	9	9	24
1,2,9,12-A_4B_9	2	20	20	1,2,3,9,10,13-B_6 A_7	9	9	24
1,2,8,10-A_4B_9	1	19	22	1,2,4,7,9,13-B_6A_7	9	9	24
1,2,3,4,5-A_5B_8	7	19	16	1,2,4,7,12,13-B_6A_7	9	9	24
1,2,3,4,9-A_5B_8	6	18	18	1,2,4,9,11,13-B_6A_7	9	9	24
1,2,3,4,10-A_5B_8	5	17	20	1,2,4,7,10,13-B_6A_7	8	8	26
1,2,3,5,8-A_5B_8	5	17	20	1,2,4,10,12,13-B_6A_7	8	8	26
1,2,3,5,9-A_5B_8	5	17	20	1,2,3,4,13-B_5A_8	15	9	18
1,2,3,5,10-A_5B_8	5	17	20	1,2,3,5,13-B_5A_8	14	8	20
1,2,4,7,8-A_5B_8	5	17	20	1,2,3,9,13-B_5A_8	13	7	22
1,2,3,5,12-A_5B_8	4	16	22	1,2,4,7,13-B_5A_8	13	7	22
1,2,3,9,10-A_5B_8	4	16	22	1,2,4,9,13-B_5A_8	13	7	22
1,2,4,7,9-A_5B_8	4	16	22	1,2,4,11,13-B_5A_8	13	7	22
1,2,4,7,12-A_5B_8	4	16	22	1,2,4,10,13-B_5A_8	12	6	24
1,2,4,9,11-A_5B_8	4	16	22	1,2,4,12,13 B_5A_8	12	6	24
1,2,4,7,10-A_5B_8	3	15	24	1,2,8,9,13-B_5A_8	12	6	24
1,2,4,10,12-A_5B_8	3	15	24	1,2,8,12,13-B_5A_8	12	6	24
1,2,3,4,5,6-A_6B_7	10	16	16	1,2,9,12,13-B_5A_8	12	6	24
1,2,3,4,5,7-A_6B_7	9	15	18	1,2,8,10,13-B_5A_8	11	5	26
1,2,3,4,5,8-A_6B_7	9	15	18	1,2,3,13-B_4A_9	18	6	18
1,2,3,4,5,9-A_6B_7	9	15	18	1,2,4,13-B_4A_9	17	5	20
1,2,3,4,5,10-A_6B_7	8	14	20	1,2,8,13-B_4A_9	16	4	22
1,2,3,4,5,11-A_6B_7	8	14	20	1,2,9,13-B_4A_9	16	4	22
1,2,3,4,5,12 A_6B_7	7	13	22	1,7,9,13-B_4A_9	15	3	24
1,2,3,4,9,10-A_6B_7	7	13	22	1,2,13-B_3A_{10}	21	3	18
1,2,3,4,9,11-A_6B_7	7	13	22	1,7,13-B_3A_{10}	20	2	20
1,2,3,4,9,12-A_6B_7	7	13	22	1,12,13-B_3A_{10}	20	2	20
1,2,3,5,8,9-A_6B_7	7	13	22	1,13-B_2A_{11}	25	1	16
1,2,3,5,9,10-A_6B_7	7	13	22	13-BA_{12}	30	0	12

contributions from each type of bond in the cluster which in turn can be obtained by multiplying the numbers of bonds (N_{AA}, N_{BB}, and N_{AB} for a binary system) of each type (AA, BB, and AB, respectively) by the corresponding bond energies (E_{AA}, E_{BB}, and E_{AB}, respectively) within the cluster core, as follows:

$$E_{\text{total}} = N_{AA}E_{AA} + N_{BB}E_{BB} + N_{AB}E_{AB} \tag{1}$$

Here, we make use of bond energies E_{ij} where i,j = A or B (ref 18) and Pauling's electronegativity listed in the Appendix. The bond energies of homonuclear bonds involving main-group elements can be found in the literature (see, e.g., ref 27). The homonuclear metallic bond energies can be estimated from the cohesive energies of bulk metal as prescribed in ref 18.

The energy of a heteronuclear bond of AB type can be determined by eq 2 for main-group elements and by eq 3 for transition metals:

$$E_{AB} = \frac{1}{2}(E_{AA} + E_{BB}) + 96.23(\chi_A - \chi_B)^2 \text{ for main-group elements} \tag{2}$$

$$E_{AB} = \frac{1}{2}(E_{AA} + E_{BB}) + 96.23((\chi_A - \chi_B)/3)^2 \text{ for transition metals} \tag{3}$$

Here, E_{AA} and E_{BB} are the covalent bond energies, and χ_A and χ_B are Pauling's electronegativities[28] for the corresponding elements. The second term in eq 2 or 3 is due to the ionic character of the covalent bond caused by the disparity of the electronegativities of the constituents. The ionic character provides an extra stabilization energy to the bond.

Knowing the energies of homonuclear (AA and BB) and heteronuclear (AB) bonds, we can now calculate the energy of clusters of other configurations via eq 1 on the basis of

---

(27) Huheey, J. E.; Keither, E. A.; Keither, R. L. *Inorganic Chemistry. Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993.

(28) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Table 4. Numbers of AA (N_{AA}), BB (N_{BB}), and AB (N_{AB}) Bonds for A-Centered Binary Icosahedral A_nB_{13-n} Clusters

A-centered icosahedral cluster	N_{AA}	N_{BB}	N_{AB}	A-centered icosahedral cluster	N_{AA}	N_{BB}	N_{AB}
13- AB_{12}	0	30	12	1,2,3,4,10,12-B_6A_7	12	6	24
1,13-A_2B_{11}	1	25	16	1,2,3,5,8,10-B_6A_7	12	6	24
1,2,13-A_3B_{10}	3	21	18	1,2,3,5,8,11-B_6A_7	12	6	24
1,7,13-A_3B_{10}	2	20	20	1,2,3,5,8,12-B_6A_7	12	6	24
1,12,13-A_3B_{10}	2	20	20	1,2,3,5,9,12-B_6A_7	12	6	24
1,2,3,13-A_4B_9	6	18	18	1,2,3,5,10,12-B_6A_7	12	6	24
1,2,4,13-A_4B_9	5	17	20	1,2,3,9,10,12-B_6A_7	12	6	24
1,2,8,13-A_4B_9	4	16	22	1,2,4,7,9,12- B_6A_7	12	6	24
1,2,9,13-A_4B_9	4	16	22	1,2,4,9,11,12-B_6A_7	12	6	24
1,7,9,13-A_4B_9	3	15	24	1,2,4,7,8,10-B_6A_7	11	5	26
1,2,3,4,13-A_5B_8	9	15	18	1,2,4,7,9,10-B_6A_7	11	5	26
1,2,3,5,13-A_5B_8	8	14	20	1,2,4,7,10,12-B_6A_7	11	5	26
1,2,3,9,13-A_5B_8	7	13	22	1,2,3,4,5-B_5A_8	19	7	16
1,2,4,7,13-A_5B_8	7	13	22	1,2,3,4,9-B_5A_8	18	6	18
1,2,4,9,13-A_5B_8	7	13	22	1,2,3,4,10-B_5A_8	17	5	20
1,2,4,11,13-A_5B_8	7	13	22	1,2,3,5,8-B_5A_8	17	5	20
1,2,4,10,13-A_5B_8	6	12	24	1,2,3,5,9-B_5A_8	17	5	20
1,2,4,12,13-A_5B_8	6	12	24	1,2,3,5,10-B_5A_8	17	5	20
1,2,8,9,13-A_5B_8	6	12	24	1,2,4,7,8-B_5A_8	17	5	20
1,2,8,12,13-A_5B_8	6	12	24	1,2,3,5,12-B_5A_8	16	4	22
1,2,9,12,13-A_5B_8	6	12	24	1,2,3,9,10-B_5A_8	16	4	22
1,2,8,10,13-A_5B_8	5	11	26	1,2,4,7,9-B_5A_8	16	4	22
1,2,3,4,5,13-A_6B_7	12	12	18	1,2,4,7,12-B_5A_8	16	4	22
1,2,3,4,9,13-A_6B_7	11	11	20	1,2,4,9,11-B_5A_8	16	4	22
1,2,3,4,10,13-A_6B_7	10	10	22	1,2,4,7,10-B_5A_8	15	3	24
1,2,3,5,8,13-A_6B_7	10	10	22	1,2,4,10,12-B_5A_8	15	3	24
1,2,3,5,9,13-A_6B_7	10	10	22	1,2,3,4-B_4A_9	23	5	14
1,2,3,5,10,13-A_6B_7	10	10	22	1,2,3,5-B_4A_9	22	4	16
1,2,4,7,8,13-A_6B_7	10	10	22	1,2,3,9-B_4A_9	21	3	18
1,2,3,5,12,13-A_6B_7	9	9	24	1,2,4,7-B_4A_9	21	3	18
1,2,3,9,10,13-A_6B_7	9	9	24	1,2,4,9-B_4A_9	21	3	18
1,2,4,7,9,13-A_6B_7	9	9	24	1,2,4,11-B_4A_9	21	3	18
1,2,4,7,12,13-A_6B_7	9	9	24	1,2,4,10-B_4A_9	20	2	20
1,2,4,9,11,13-A_6B_7	9	9	24	1,2,4,12-B_4A_9	20	2	20
1,2,4,7,10,13-A_6B_7	8	8	26	1,2,8,9- B_4A_9	20	2	20
1,2,4,10,12,13-A_6B_7	8	8	26	1,2,8,12-B_4A_9	20	2	20
1,2,3,4,5,6-B_6A_7	16	10	16	1,2,9,12-B_4A_9	20	2	20
1,2,3,4,5,7-B_6A_7	15	9	18	1,2,8,10-B_4A_9	19	1	22
1,2,3,4,5,8-B_6A_7	15	9	18	1,2,3-B_3A_{10}	26	2	14
1,2,3,4,5,9-B_6A_7	15	9	18	1,2,4-B_3A_{10}	26	2	14
1,2,3,4,5,10-B_6A_7	14	8	20	1,2,8-B_3A_{10}	25	1	16
1,2,3,4,5,11-B_6A_7	14	8	20	1,2,9-B_3A_{10}	25	1	16
1,2,3,4,5,12 B_6A_7	13	7	22	1,7,9-B_3A_{10}	24	0	18
1,2,3,4,9,10-B_6A_7	13	7	22	1,2-B_2A_{11}	31	1	10
1,2,3,4,9,11-B_6A_7	13	7	22	1,7-B_2A_{11}	30	0	12
1,2,3,4,9,12-B_6A_7	13	7	22	1,12-B_2A_{11}	30	0	12
1,2,3,5,8,9-B_6A_7	13	7	22	1-BA_{12}	36	0	6
1,2,3,5,9,10-B_6A_7	13	7	22	A_{13}	42	0	0

the parameters listed in the Appendix. The calculations were performed for noncentered icosahedral A_nB_{12-n} clusters comprising B, C, N, and S, as well as B- and A-centered icosahedral A_nB_{13-n} clusters that consist of Au, Ag, Ni, and Pt atoms. The results, relative to the most stable configurations, are tabulated in Tables 5−7, respectively. The total bond energies for the latter B- and A-centered icosahedral A_nB_{13-n} clusters are listed in Tables S1 and S2, respectively, and compared with results of our previous calculations using the L-J method (ref 18).

It should be noted that the total bond energy E_{total} (eq 1 and Tables 5−7 in this paper) differs from the total energy U_{total} (Tables S1 and S2 in this paper and eq 5 and 7 as well as Table 3 in ref 18) by a sign change: $U_{total} = -E_{total}$. Hence, the energy difference between 2 positional isomers, m and n, is given by $U_m - U_n = E_n - E_m$. A larger E_{total} value means a more negative U_{total} value which implies a greater stability.

Table 5. Calculated Relative Bond Energies (kJ/mol) of All Possible Positional Isomers of Noncentered Binary (A−B = C−B, N−B, and S−B) Icosahedral A_nB_{12-n} Clusters with Respect to the Most Stable Positional Isomers[a]

count	noncentered	N_{AA}[b]	A = C B = B	A = N B = B	A = S B = B
1	B_{12}	0	0	0	0
1	AB_{11}	0	0	0	0
1	A_2B_{10}	1	50.06	192.46	56.12
2	A_2B_{10}	0	0	0	0
1	A_3B_9	3	150.18	577.38	168.36
1	A_3B_9	2	100.12	384.92	112.24
2	A_3B_9	1	50.06	192.46	56.12
1	A_3B_9	0	0	0	0
1	A_4B_8	5	200.24	769.84	224.49
1	A_4B_8	4	150.18	577.38	168.36
4	A_4B_8	3	100.12	384.92	112.24
5	A_4B_8	2	50.06	192.46	56.12
1	A_4B_8	1	0	0	0
1	A_5B_7	7	200.24	769.84	224.49
1	A_5B_7	6	150.18	577.38	168.36
5	A_5B_7	5	100.12	384.92	112.24
5	A_5B_7	4	50.06	192.46	56.12
2	A_5B_7	3	0	0	0
1	A_6B_6	10	250.29	962.30	280.61
3	A_6B_6	9	200.24	769.84	224.49
2	A_6B_6	8	150.18	577.38	168.36
6	A_6B_6	7	100.12	384.92	112.24
9	A_6B_6	6	50.06	192.46	56.12
3	A_6B_6	5	0	0	0
count	noncentered	N_{BB}[c]	A = C B = B	A = N B = B	A = S B = B
1	B_5A_7	7	200.24	769.84	224.49
1	B_5A_7	6	150.18	577.38	168.36
5	B_5A_7	5	100.12	384.92	112.24
5	B_5A_7	4	50.06	192.46	56.12
2	B_5A_7	3	0	0	0
1	B_4A_8	5	200.24	769.84	224.49
1	B_4A_8	4	150.18	577.38	168.36
4	B_4A_8	3	100.12	384.92	112.24
5	B_4A_8	2	50.06	192.46	56.12
1	B_4A_8	1	0	0	0
1	B_3A_9	3	150.18	577.38	168.36
1	B_3A_9	2	100.12	384.92	112.24
2	B_3A_9	1	50.06	192.46	56.12
1	B_3A_9	0	0	0	0
1	B_2A_{10}	1	50.06	192.46	56.12
2	B_2A_{10}	0	0	0	0
1	BA_{11}	0	0	0	0
1	A_{12}	0	0	0	0

[a] Relative to the most stable positional isomers which are designated as zeros. [b] The relative energetics can be determined by the numbers of the minority bonds (i.e., A−A bonds for A_nB_{12-n} where $n < 6$). [c] The relative energetics can be determined by the numbers of the minority bonds (i.e., B−B bonds for B_nA_{12-n} where $n < 6$). Note that for B_6A_6, $N_{AA} = N_{BB}$.

Results

The numbers of A−A, B−B, and A−B bonds for all possible configurations of noncentered, B-centered, and A-centered icosahedral binary clusters, calculated from the adjacent matrices as described previously, are listed in Tables 2−4, respectively. Note that one half of Table 2 can be obtained by interchanging atom types A and B of the other half. Interchanging atom types A and B of one half of Table 3 (B-centered), however, produces the other half of Table 4 (A-centered), and vice versa. To avoid confusion and to facilitate comparison with our prior work, complete tables are provided here. Using these numbers of bonds and the bond energies calculated on the basis of eqs 2 and 3, the “total bond energy”, E_{total}, for a particular positional isomer can readily be computed. We shall discuss a few examples next.

Table 6. Calculated Relative Metallic Energies (kJ/mol) of All Possible Positional Isomers of B-Centered Binary (A−B = Ag−Au, Ni−Au, and Pt−Au) Icosahedral A_nB_{13-n} Clusters with Respect to the Most Stable Positional Isomers[a]

count	B-centered	N_{AA}[b]	A = Ag B = Au	A = Ni B = Au	A = Pt B = Au
1	B_{13}	0	0	0	0
1	AB_{12}	0	0	0	0
1	A_2B_{11}	1	7.96	8.49	1.44
2	A_2B_{11}	0	0	0	0
1	A_3B_{10}	3	23.87	25.46	4.34
1	A_3B_{10}	2	15.92	16.97	2.89
2	A_3B_{10}	1	7.96	8.48	1.45
1	A_3B_{10}	0	0	0	0
1	A_4B_9	5	31.83	33.96	5.78
1	A_4B_9	4	23.87	25.47	4.34
4	A_4B_9	3	15.91	16.98	2.89
5	A_4B_9	2	7.96	8.49	1.45
1	A_4B_9	1	0	0	0
1	A_5B_8	7	31.82	33.96	5.78
1	A_5B_8	6	23.87	25.47	4.33
5	A_5B_8	5	15.91	16.98	2.89
5	A_5B_8	4	7.95	8.49	1.44
2	A_5B_8	3	0	0	0
1	A_6B_7	10	39.79	42.44	7.23
3	A_6B_7	9	31.82	33.96	5.79
2	A_6B_7	8	23.87	25.47	4.34
6	A_6B_7	7	15.92	16.98	2.89
9	A_6B_7	6	7.96	8.49	1.45
3	A_6B_7	5	0	0	0

count	B-centered	N_{BB}[c]	A = Ag B = Au	A = Ni B = Au	A = Pt B = Au
1	B_6A_7	12	31.83	33.96	5.79
1	B_6A_7	11	23.88	25.47	4.34
5	B_6A_7	10	15.92	16.98	2.90
5	B_6A_7	9	7.96	8.49	1.45
2	B_6A_7	8	0	0	0
1	B_5A_8	9	31.82	33.95	5.78
1	B_5A_8	8	23.87	25.46	4.33
4	B_5A_8	7	15.91	16.97	2.89
5	B_5A_8	6	7.95	8.49	1.44
1	B_5A_8	5	0	0	0
1	B_4A_9	6	23.87	25.46	4.34
1	B_4A_9	5	15.91	16.97	2.90
2	B_4A_9	4	7.95	8.48	1.45
1	B_4A_9	3	0	0	0
1	B_3A_{10}	3	7.96	8.49	1.44
2	B_3A_{10}	2	0	0	0
1	B_2A_{11}	1	0	0	0
1	BA_{12}	0	0	0	0

[a] Relative to the most stable positional isomers which are designated as zeros. [b] The relative energetics can be determined by the numbers of the minority bonds (i.e., A−A bonds for A_nB_{13-n} where $n < 7$). [c] The relative energetics can be determined by the numbers of the minority bonds (i.e., B−B bonds for B_nA_{13-n} where $n < 7$). Note that for B-centered B_6A_7, $N_{AA} = N_{BB}$.

Table 7. Calculated Relative Metallic Energies (kJ/mol) of All Possible Positional Isomers of A-Centered Binary (A−B = Ag−Au, Ni−Au, and Pt−Au) Icosahedral A_nB_{13-n} Clusters with Respect to the Most Stable Positional Isomers[a]

count	A-centered	N_{AA}[b]	A = Ag B = Au	A = Ni B = Au	A = Pt B = Au
1	AB_{12}	0	0	0	0
1	A_2B_{11}	1	0	0	0
1	A_3B_{10}	3	7.95	8.49	1.44
2	A_3B_{10}	2	0	0	0
1	A_4B_9	6	23.87	25.46	4.33
1	A_4B_9	5	15.91	16.97	2.89
2	A_4B_9	4	7.95	8.48	1.44
1	A_4B_9	3	0	0	0
1	A_5B_8	9	31.82	33.96	5.79
1	A_5B_8	8	23.87	25.47	4.34
4	A_5B_8	7	15.91	16.98	2.89
5	A_5B_8	6	7.95	8.49	1.45
1	A_5B_8	5	0	0	0
1	A_6B_7	12	31.81	33.96	5.79
1	A_6B_7	11	23.86	25.47	4.34
5	A_6B_7	10	15.90	16.98	2.90
5	A_6B_7	9	7.94	8.49	1.45
2	A_6B_7	8	0	0	0

count	B-centered	N_{BB}[c]	A = Ag B = Au	A = Ni B = Au	A = Pt B = Au
1	B_6A_7	10	39.75	42.43	7.23
3	B_6A_7	9	31.80	33.95	5.78
2	B_6A_7	8	23.85	25.46	4.33
6	B_6A_7	7	15.90	16.97	2.89
9	B_6A_7	6	7.95	8.49	1.44
3	B_6A_7	5	0	0	0
1	B_5A_8	7	31.80	33.95	5.79
1	B_5A_8	6	23.85	25.46	4.34
5	B_5A_8	5	15.90	16.97	2.90
5	B_5A_8	4	7.95	8.48	1.45
2	B_5A_8	3	0	0	0
1	B_4A_9	5	31.83	33.95	5.78
1	B_4A_9	4	23.87	25.46	4.34
4	B_4A_9	3	15.91	16.97	2.89
5	B_4A_9	2	7.96	8.48	1.45
1	B_4A_9	1	0	0	0
1	B_3A_{10}	3	23.88	25.46	4.34
1	B_3A_{10}	2	15.92	16.97	2.89
2	B_3A_{10}	1	7.96	8.48	1.45
1	B_3A_{10}	0	0	0	0
1	B_2A_{11}	1	7.96	8.49	1.45
2	B_2A_{11}	0	0	0	0
1	BA_{12}	0	0	0	0
1	A_{13}	0	0	0	0

[a] Relative to the most stable positional isomers which are designated as zeros. [b] The relative energetics can be determined by the numbers of the minority bonds (i.e., A−A bonds, third row) for A_nB_{13-n} where $n < 7$. [c] The relative energetics can be determined by the numbers of the minority bonds (i.e., B−B bonds, third row) for B_nA_{13-n} where $n < 7$. Note that for A-centered A_6B_7, $N_{AA} = N_{BB}$.

For the noncentered icosahedral cluster, the total number of bonds is 30, so it follows from Table 2 that, for B_{12}, the number of AA bonds is 0, the number of BB bonds is 30, and the number of AB bonds is 0. Thus, the total energy E of an icosahedral cluster B_{12} is given by $E = 30E_{BB}$ where E_{BB} is the homonuclear metallic bond energy for the B−B bond as listed in the Appendix. If we now substitute the atom of the B type at position 1 with an atom of the A type, giving rise to 1-AB_{11}, it will form 5 bonds of type AB with the B atoms at positions 2−6. At the same time, the total number of bonds of type BB will decrease by 5, or a total of $30 - 5 = 25$. This is reflected in the next row of Table 2 that lists the numbers of AA, BB, and AB bonds as 0, 25, and 5, respectively, for the 1-AB_{11} configuration. The total energy for 1-AB_{11} is $E = 25E_{BB} + 5E_{AB}$. There are 3 unique positional isomers for the A_2B_{10} system. The placement of the second atom of type A in position 2 gives rise to the 1,2-A_2B_{10} configuration. One bond of type AA between atoms of type A at positions 1 and 2 is formed. An atom of type A at position 1 will form bonds of the AB type with the atoms of type B at positions 3−6: a total of 4 AB bonds. An atom of type A at position 2 will form bonds of type AB with the atoms of the B type at positions 3, 6, 7, and 11: a total of 4 AB bonds. Hence, the total number of bonds of type AB formed by atoms of the type A at positions 1 and 2 with their neighbors of type B is 8. The total number of bonds of type BB will be reduced accordingly: $30 - 1 - 8 = 21$. So, for 1,2-A_2B_{10} , the numbers of AA, BB, and AB bonds are 1, 21, and 8, respectively, as listed in Table 2. The total energy for 1,2-AB_{11} is $E = E_{AA} + 21E_{BB} +$

$8E_{AB}$. For the 1,7-A_2B_{10} and 1,12-A_2B_{10} configurations, there are no AA bonds (two fragments of the minority atoms); each minority A atom makes 5 AB bonds or a total of 10 AB bonds. The number of BB bonds is reduced to $30 - 10 = 20$. Hence, the numbers of AA, BB, and AB bonds are 0, 20, and 10, respectively. The total energy for either 1,7-A_2B_{10} or 1,12-A_2B_{10} is $E = 20E_{BB} + 10E_{AB}$. It can be seen that 1,7-A_2B_{10} and 1,12-A_2B_{10} positional isomers are of same energy in the spirit of the tight-binding approach. A similar argument applies to other positional isomeric configurations listed in Table 2.

We shall now turn our attention to the centered icosahedral cluster. The total number of bonds in the centered icosahedral cluster is 42, 30 on the surface of the icosahedron and 12 connecting the central atom with the 12 surface atoms. So, it follows from Table 3 that for the B-centered cluster B_{13} the number of AA bonds is 0, the number of BB bonds is 42, and the number of AB bonds is 0. For example, the total energy E of the cluster of configuration Au_{13} can be calculated by $E = 42E_{AuAu}$. Here, 42 is the number of Au−Au bonds and E_{AuAu} is the Au−Au homonuclear metallic bond energy as listed in the Appendix for the B_{13} configuration. If we now substitute the atom of the B type at position 1 by an atom of the A type, it will form 6 bonds of AB type with the B atoms at positions 2−6 and 13. At the same time, the total number of bonds of the BB type will decrease by 6 bonds, or a total of $42 - 6 = 36$. This is reflected in the next row of the table that lists the numbers of bonds for the 1-AB_{12} configuration. The total energy for 1-AB_{12} will be $E = 36E_{BB} + 6E_{AB}$. The placement of the second atom of type A to position 2 gives rise to the 1,2-A_2B_{11} configuration. One bond of type AA between atoms of the A type at positions 1 and 2 will be created. An atom of type A at position 1 will form bonds of the AB type with atoms of the B type at positions 3−6 and 13: a total of 5 AB bonds. An atom of type A at position 2 will form bonds of the AB type with atoms of the B type at positions 3, 6, 7, 11, and 13: a total of 5 AB bonds. Hence, the total number of bonds of the AB type formed by atoms of type A at positions 1 and 2 with their neighbors of type B is 10. The total number of bonds of the BB type will be then $42 - 1 - 10 = 31$. So, for the third configuration, 1,2-A_2B_{11}, from Table 3, the numbers of AA, BB, and AB bonds are 1, 31, and 10, respectively. Thus, the total energy for 1,2-AB_{13} is $E = E_{AA} + 31E_{BB} + 10E_{AB}$. For the two-fragment positional isomers 1,7-A_2B_{11} and 1,12-A_2B_{11}, there are no AA bonds; each minority A atom makes 6 AB bonds (5 to the surface and 1 to the central B atoms) or a total of 12 AB bonds. The number of BB bonds is thereby reduced to $42 - 12 = 30$. Therefore, the numbers of AA, BB, and AB bonds are 0, 30, and 12, respectively. The total energy for either 1,7-AB_{12} or 1,12-AB_{12} is $E = 30E_{BB} + 12E_{AB}$. A similar argument applies to other positional isomeric configurations listed in Table 3. The corresponding information for the A-centered icosahedral clusters is listed in Table 4.

Stepwise Progression of Bond Energies. It can be seen from Tables 2−4 that the total bond energies of the positional isomers of a given noncentered A_nB_{12-n} or a centered A_nB_{13-n} icosahedral cluster are uniquely determined by a set of A−A, B−B, and A−B bonds. As the numbers of these bonds vary in a systematic manner, the total bond energies exhibit a stepwise progression, as tabulated in Tables 2−4 and illustrated in Figures 2 and 3 for Ag_4Au_9 and Ag_6Au_7, respectively. In other words, each step is characterized by a unique set of A−A, B−B, and A−B bonds which in turn determine total bond energies and hence the stability of the type. The step formation implies that the positional isomers of a given A_nB_{12-n} or A_nB_{13-n} icosahedral cluster can be categorized by the sets of numbers of A−A, B−B, and A−B bonds that uniquely determine their total bond energies. For the sake of convenience, we shall use the number of the minority (either A−A or B−B) bonds (see column 3 of Tables 5−7) to specify each positional isomeric type. For example, for a B-centered icosahedral A_4B_9 cluster (see Table 3 and Figure 2), there are 5 types, with 1, 1, 4, 5, and 1 positional isomers, possessing 5, 4, 3, 2, and 1 A−A (minority) bonds, respectively. These data are listed in the first and third columns of Table 6. The stability increases with a decreasing number of A−A (or B−B) bonds, or, equivalently, an increasing number of A−B bonds (because of the ionic contributions from the A−B bonds; see the heterobond rule to be discussed later). The last one, 1,2,8,-10-A_4B_9, has the smallest numbers of A−A and B−B bonds but the largest number of A−B bonds and, hence, is the most stable structure. The opposite is true for the first type, 1,2,3,4-A_4B_9, which is the least stable structure. The 5 types correspond to the 5 steps in Figure 2. A similar argument applies to Figure 3 which will be discussed later.

The calculated total bond energies for the binary main-group A−B = C−B, N−B, and S−B noncentered A_nB_{12-n} icosahedral cluster systems based on the TBAM approach are tabulated in Table 5. Of the three systems, carboranes are the most common, and only with a small number of carbon atoms. In contrast, most of the N−B and S−B icosahedral clusters are presently unknown. They are included here to provide a comparison of constituents with different bond energies and electronegativities. The calculated total bond energies for the binary A−B = Ag−Au, Ni−Au, and Pt−Au centered icosahedral A_nB_{13-n} cluster systems based on the TBAM approach are tabulated in Tables 6 (B-centered) and 7 (A-centered). For the sake of clarity, the listed energies are relative to the most stable positional isomeric type (the last one under each category, as discussed in the previous paragraph) which is assigned a value of zero. Table 6 (B-centered) lists binding energies with the Au atom (B type) placed at position 13, that is, in the center of the cluster, while Table 7 (A-centered) lists binding energies for clusters with Ag, Ni, or Pt atoms (A type) placed at the center of the cluster.

A detailed examination of Tables 5−7 revealed that the energy differences between the various positional isomeric types are in steps of η where

$$\eta = 2E_{AB} - (E_{AA} + E_{BB}) \qquad (4)$$

In fact, η is simply twice the ionic contribution to the covalent A−B bond if one substitutes eq 2 or 3 into eq 4:

$$\eta = 2 \times 96.23(\chi_A - \chi_B)^2 \text{ for main-group elements} \quad (5)$$

$$\eta = 2 \times 96.23((\chi_A - \chi_B)/3)^2 \text{ for transition metals} \quad (6)$$

In other words, replacements of two homonuclear, A−A and B−B, bonds by 2 heteronuclear A−B bonds increase the total bond energy (enhancing stability) by η. For example, η = 50.06, 192.46, and 56.12 kJ/mol for the A−B = C−B, N−B, S−B pairs, respectively, and can be calculated from eq 5 in agreement with the results listed in Table 5. Similarly, η = 7.96, 8.49, 1.45 kJ/mol for the A−B = Ag−Au, Ni−Au, and Pt−Au pairs, respectively, and can be calculated from eq 6 in agreement with the results listed in Tables 6 and 7. Apparently, the η values for the main-group clusters are substantially larger than the η values for the transition-metal clusters, suggesting that the energetic differences between the various positional isomers are much greater for the former. We shall come back to this point in later discussions.

Comparison of TBAM and L-J Methods. The results from the tight-binding adjacent matrix (TBAM) method (this work) are compared with the results based on Lennard-Jones calculations[18] in Tables S1 (B-centered) and S2 (A-centered) of the Supporting Information. The energies listed in these tables differ from those reported in ref 18 in that they are in kilojoules per mole (this work) instead of kilocalories per mole (Table 3 of ref 18). The conversion factor for the two units is 1 kcal = 4.184 kJ. In both cases, the most stable (the lowest binding energy) are marked with an asterisk. The positional isomers in Tables S1 and S2 are arranged in exactly the same order as those in ref 18 for ease of comparison. This particular ordering is different from that in Tables 2−6 of this paper for reasons explained earlier.

As we can see, in most instances TBAM and L-J methods predict the same ordering of the stability of the positional isomers. However, the "relaxed cluster" molecular mechanics L-J calculations[18] gave rise to a lower binding energy for the same configuration than the TBAM method presented here. Nevertheless, the trends are nearly parallel in all cases. In other words, the predicted relative stabilities based on the calculated relative total bond energies of the different configurations by the two methods follow the same order.

If we define γ as the ratio of the total bond energy calculated using the "relaxed" L-J method to that obtained by the TBAM approach (this work), we find γ to be nearly constant for all the configurations. Specifically, γ equals 0.95, 0.93−1.00, and 0.94 for the Ag−Au, Ni−Au, and Pt−Au systems, respectively. Hence, the results based on L-J calculations can be reproduced reasonably well by multiplying the TBAM results with the factor γ. The net result is the savings of many man-months of tedious calculations.

Discussion

The TBAM method differs from the L-J method (ref 18) in two aspects. First, while the TBAM approach takes into account only the nearest-neighbor bonds, the L-J method includes not only nearest-neighbor interactions but also interactions between all pairs of atoms in the calculations. Second, while the TBAM scheme requires a simple sum of the multiplication products of the numbers of bonds with the corresponding bond energies for each type of bonds within the cluster, the L-J method minimizes the energy and, at the same time, optimizes the geometry of the cluster. Thus, the TBAM method does not require tedious time-consuming calculations that require a computer by bypassing the energy minimization and geometry optimization. In fact, it can readily be performed by hand if the number of bonds and the corresponding bond energy for each type of bonds in the cluster are known. Fortunately, as illustrated in Figures 1−4 and Tables S1 and S2 and as discussed in the previous section, the trends of the total bond energies obtained by the two methods are nearly parallel in all cases. Hence, the relative stability trends predicted by the two methods are the same and agree with the experimental results.[15−17]

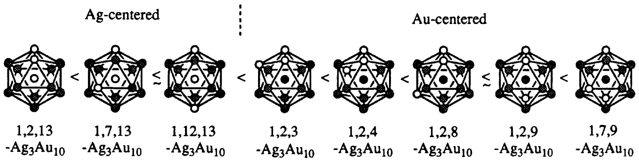

Figure 1. Relative stabilities of Ag_3Au_{10} positional isomers.

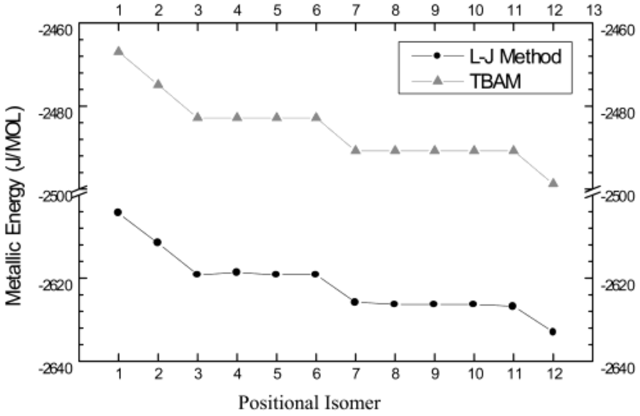

Figure 2. Total bond energies of the various positional isomers of Au-centered icosahedral Ag_4Au_9 clusters calculated using TBAM (this work) and L-J methods (ref 18). From left to right: (1) 1,2,3,4-Ag_4Au_9; (2) 1,2,3,5-Ag_4Au_9; (3) 1,2,3,9-Ag_4Au_9; (4) 1,2,4,7-Ag_4Au_9; (5) 1,2,4,9-Ag_4Au_9; (6) 1,2,4,11-Ag_4Au_9; (7) 1,2,4,10-Ag_4Au_9; (8) 1,2,4,12-Ag_4Au_9; (9) 1,2,8,9-Ag_4Au_9; (10) 1,2,8,12-Ag_4Au_9; (11) 1,2,9,12-Ag_4Au_9; (12) 1,2,8,10-Ag_4Au_9.

Because the TBAM approach takes into account only the nearest neighbor bonds, it cannot differentiate positional isomers whose energy difference depends on long-range interactions (i.e., other than nearest-neighbor interactions). For instance, while it correctly predicted that 1,7- and 1,-12-$C_2B_{10}H_{12}$ are substantially more stable than 1,2-$C_2B_{10}H_{12}$ (see Table 5), it cannot differentiate between 1,7-$C_2B_{10}H_{12}$ and 1,12-$C_2B_{10}H_{12}$ because they differ in interactions other than the nearest-neighbor interactions. The inability to differentiate positional isomers that differ in long-range interactions other than nearest-neighbor interactions is also true for other kinds of three-dimensional Huckel-type theory.[23] Experimentally, 1,2-$C_2B_{10}H_{12}$ is the kinetically favored product whereas 1,12-$C_2B_{10}H_{12}$ is the thermodynamically most stable compound. In fact, 1,2-$C_2B_{10}H_{12}$ can be transformed thermally (at 470 °C) to 1,7-$C_2B_{10}H_{12}$ which

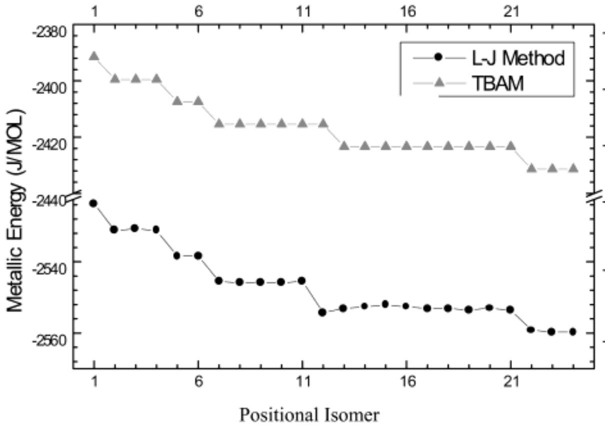

Figure 3. Total bond energies of the various positional isomers of Au-centered icosahedral Ag_6Au_7 clusters calculated using TBAM (this work) and L-J methods (ref 18). From left to right: (1) 1,2,3,4,5,6-Ag_6Au_7; (2) 1,2,3,4,5,7-Ag_6Au_7; (3) 1,2,3,4,5,8-Ag_6Au_7; (4) 1,2,3,4,5,9-Ag_6Au_7; (5) 1,2,3,4,5,10-Ag_6Au_7; (6) 1,2,3,4,5,11-Ag_6Au_7; (7) 1,2,3,4,5,12-Ag_6Au_7; (8) 1,2,3,4,9,10-Ag_6Au_7; (9) 1,2,3,4,9,11-Ag_6Au_7; (10) 1,2,3,4,9,12-Ag_6Au_7; (11) 1,2,3,5,8,9-Ag_6Au_7; (12) 1,2,3,5,9,10-Ag_6Au_7; (13) 1,2,3,4,10,12-Ag_6Au_7; (14) 1,2,3,5,8,10-Ag_6Au_7; (15) 1,2,3,5,8,11-Ag_6Au_7; (16) 1,2,3,5,8,12-Ag_6Au_7; (17) 1,2,3,5,9,12-Ag_6Au_7; (18) 1,2,3,5,10,12-Ag_6Au_7; (19) 1,2,3,9,10,12-Ag_6Au_7; (20) 1,2,4,7,9,12-Ag_6Au_7; (21) 1,2,4,9,11,12-Ag_6Au_7; (22) 1,2,4,7,8,10-Ag_6Au_7; (23) 1,2,4,7,9,10-Ag_6Au_7; (24) 1,2,4,7,10,12-Ag_6Au_7.

in turn can be transformed to 1,12-$C_2B_{10}H_{12}$ at 615 °C, indicating the thermodynamic stability trend of 1,2-$C_2B_{10}H_{12}$ $\ll$ 1,7-$C_2B_{10}H_{12}$ < 1,12-$C_2B_{10}H_{12}$.[29] Indeed, ab initio calculations[24] indicated that relative energies of the 3 positional isomers are, in the same order, $35.9 \gg 4.6 > 0$ kcal/mol.

As was pointed out previously, we do not expect the absolute energies calculated using these two different methods to be the same. In fact, because the TBAM method bypasses the energy minimization, one would expect the energies obtained using the TBAM method to be higher that the energies obtained using the L-J method.[18] Indeed, as depicted in Figures 2 and 3 for the Au-centered icosahedral Ag_4Au_9 and Ag_6Au_7 clusters, respectively, the total bond energies obtained by the TBAM method are significantly larger than the corresponding values obtained by the L-J method. Fortunately, the two curves showed the same relative trends.

The most stable positional isomers of the three icosahedral series $A_nB_{13-}n$ (where $n = 0-12$) are depicted graphically in Figure 4: the Au-centered icosahedral $Ag_nAu_{13-}n$ (■), Ni-centered icosahedral $Au_nNi_{13-}n$ (▲), and Pt-centered icosahedral $Au_nPt_{13-}n$ (●). Note that the total bond energies of the most stable structures of the Ag-centered Ag_nAu_{13-n}, Au-centered $Au_nNi_{13-}n$, and Au-centered $Au_nPt_{13-}n$ cluster series are higher than those of the three series presented here and hence are not shown. Once again, the trends obtained by the two methods are parallel.

It should be emphasized that the TBAM approach presented in this paper ignores changes in bond energies due to bond length variations as well as the difference in bond energies between surface-to-surface and surface-to-center bonds. These approximations are justifiable on the basis of our previous calculations using the L-J method.

We shall now discuss three site preference rules as derived from our calculations. While the first two have been described previously in ref 18, the third rule is presented here for the first time.

Strong-Bond Rule: The Covalent Contribution. As was discussed in ref 18, the strong-bond rule implies that metals which are capable of forming strong metal−metal bonds tend to occupy positions of the highest "valencies" (i.e., the largest numbers of interactions). The strong-bond rule is related to the covalent contribution of the bond. In the case of an icosahedron, the center position has the maximum valency of 12. It is therefore predicted that the center position will be occupied by the "strong" metal which refers to the element forming strong bonds (large bonding energies).

The results of the TBAM calculations comply with the strong-bond rule. For example, of the 2 positional isomers of the $AgAu_{12}$ icosahedral cluster, the Au-centered positional isomer 1-$AgAu_{12}$ is more stable than the Ag-centered structure 13-$AgAu_{12}$ by 17.82 kJ/mol. This can be attributed to the fact that Au has a higher cohesive energy than Ag (see Appendix) and that there are 36 Au−Au bonds and 6 Au−Ag bonds in 1-$AgAu_{12}$ whereas there are 30 Au−Au and 12 Au−Ag bonds in 13-$AgAu_{12}$. Similarly, the Ni-centered 13-$NiAu_{12}$ is more stable than the Au-centered 1-$NiAu_{12}$ by 56.36 kJ/mol because Ni has a higher cohesive energy than Au (see Appendix).

The 3 Au-centered positional isomers (1,2-, 1,7-, and 1,-12-Ag_2Au_{11}) are more stable than the Ag-centered structure (1,13-Ag_2Au_{11}) by 16−25 kJ/mol because gold is a "stronger" metal than silver. In contrast, the Ni-centered positional isomer 1,13-Ni_2Au_{11} is substantially more stable than the 3 Au-centered positional isomers by 48.0−56.5 kJ/mol because nickel is a "stronger" metal than gold. Similar conclusions can be drawn: the 5 Au-centered Ag_3Au_{10} clusters are more stable than the 3 Ag-centered Ag_3Au_{10} clusters, as depicted in Figure 1. The reverse is true for the Ni_3Au_{10} clusters (not shown).

The same rule applies to other centered icosahedral clusters as well. For example, the $PdAu_{12}$ cluster $[(Ph_3PAu)_6(dppeAu_2)(AuCl)_4Pd]$[30] is Pd-centered because Pd is a stronger metal than Au. Furthermore, for the trimetallic Au−Ag−M (M = group 10 metals, Ni, Pd, Pt) vertex-sharing polyicosahedral clusters, the group 10 metals (which are "stronger" than the coinage metals) always occupy the center of the icosahedron as observed in a recently reported series of vertex-sharing biicosahedral Au−Ag−M (M = Ni, Pd, Pt) clusters.[31] Further examples of icosahedral clusters will be dicussed in the next subsection.

Heterobond Rule: The Ionic Contribution. As stated in ref 18, heteronuclear cluster systems tend to maximize the number of heteronuclear bonds (at the expense of the homonuclear bonds). This was coined the "heterobond" rule. The heterobond rule is related to the ionic character of the heteronuclear bond. The results of the TBAM calculations also agree with this rule. For example, of the 3 positional

---

(29) (a) Papetti, S.; Obenland, C. O.; Heying, T. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1966**, *5*, 334. (b) Sieckhaus, J. F.; Semenuk, N. S.; Knowles, T. A.; Schroeder, H. *Inorg. Chem.* **1969**, *8*, 2452.

(30) Laupp, M.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 207.

(31) (a) Teo, B. K.; Zhang, H. *J. Cluster Sci.* **2001**, *12*, 357−391. (b) Teo, B. K.; Zhang, H.; Shi, X. *Inorg. Chem.* **1994**, *33*, 4086. (c) Teo, B. K.; Zhang, H.; Shi, X. *J. Am. Chem. Soc.* **1993**, *115*, 8489.

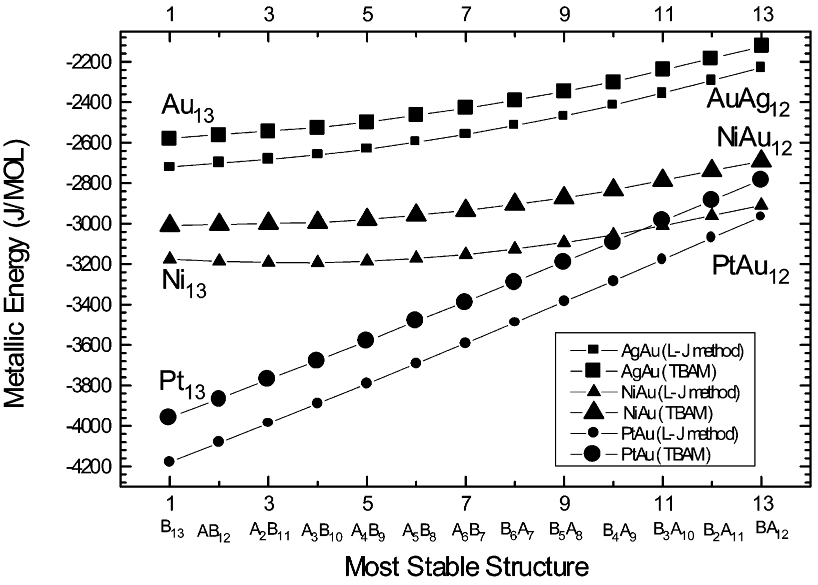

Figure 4. Total bond energies of the most stable structures of Au-centered icosahedral Ag_nAu_{13-n} (■), Ni-centered icosahedral Au_nNi_{13-n} (▲), and Pt-centered icosahedral Au_nPt_{13-n} (●) clusters calculated using TBAM (bigger symbols) and L-J methods (smaller symbols). Note that the total bond energies of the most stable structures of the Ag-centered Ag_nAu_{13-n}, Au-centered Au_nNi_{13-n}, and Au-centered Au_nPt_{13-n} cluster series (not shown) are of higher energies than those of the three series shown here.

isomers of the Au-centered Ag_2Au_{11} clusters, the 2 in which the 2 silver atoms are not neighbors (1,7- and 1,12-Ag_2Au_{11}) are more stable than the 1 (1,2-Ag_2Au_{11}) in which the 2 silver atoms are bonded to each other (as neighbors) by 8 kJ/mol.

A more useful expression of the heterobond rule is the "maximum-fragment" rule which states that positional isomers with a higher number of fragments of the minority atoms tend to be more stable. The same is also true for the TBAM results: of the 5 Au-centered Ag_3Au_{10} positional isomers in Figure 1, the one with 3 minority fragments (1,7,9-Ag_3Au_{10}) is 8 kJ/mol more stable than the two-fragment positional isomers (1,2,8- and 1,2,9-Ag_3Au_{10}) which are in turn ~8−16 kJ/mol more stable than the one-fragment positional isomers (1,2,3- and 1,2,4-Ag_3Au_{10}). The same principle applies to the 3 Ag-centered positional isomers in Figure 1 (see also Table 6).

The heterobond rule applies to other centered icosahedral clusters as well. For example, the three-fragment configuration 1,2,8,10-Ag_4Au_9 was found in $[(MePh_2P)_8Ag_4Au_9Br_4]^{+}$ [32] This is in fact the most stable structure calculated for the Ag_4Au_9 cluster as shown in Figure 4 of ref 17b. As listed in Table 5, the 12 positional isomers of the Ag_4Au_9 cluster can be categorized into 5 types (which correspond to the 5 steps in Figure 2) depending upon the number of A−A bonds (i.e., Ag−Ag bonds). Thus, there are 1, 1, 4, 5, and 1 positional isomers with 5, 4, 3, 2, and 1 A−A bonds, respectively; the last one, which has the smallest number of A−A or B−B bonds but the largest number of A−B bonds, is the most stable structure. This is consistent with the heterobond rule whereby the system tends to maximize the number of heterobonds because of the ionic character contribution to the bond energy.

Further examples of centered icosahedral clusters can be found as building blocks in a series of vertex-sharing polyicosahedral Au−Ag[33−35] and Au−Ag−M (M = Pt, Pd, Ni)[31] clusters synthesized and structurally characterized in our laboratory. As illustrated in Figure 8 of ref 18, positional isomers 1,2,4,7,8,10-, 1,2,4,7,9,12-, and 1,2,4,9,11,12-Ag_6Au_7 have been found to be the basic building units for biicosahedral,[33] triicosahedral,[34] and tetraicosahedral[34] supraclusters, respectively.

We shall now consider all possible positional isomers of a Au-centered icosahedral Ag_6Au_7 cluster. Once again, as listed in Table 3, the 24 positional isomers can be categorized into 6 types, according to the number of A−A bonds. In other words, there are 1, 3, 2, 6, 9, and 3 structures with 10, 9, 8, 7, 6, and 5 A−A bonds, in increasing order of stability, corresponding to the 6 steps in Figure 3. One of the 3 most stable positional isomers of a Ag_6Au_7 cluster, 1,2,4,7,8,10-Ag_6Au_7 of C_{5v} symmetry (Figure 8b in ref 18), has been observed as the building block in an extensive series of vertex-sharing biicosahedral clusters.[33] The 1,2,4,7,9,12-Ag_6Au_7 structure of C_{2v} symmetry is the building block for vertex-sharing triicosahedral Au−Ag clusters[34] (Figure 8c in ref 18). Likewise, the 1,2,4,9,11,12-Ag_6Au_7 structure is the building block for the vertex-sharing tetraicosahedral cluster $[(Ph_3P)_{12}Au_{22}Ag_{24}Cl_{14}]$ (Figure 8d in ref 18). These latter structures are in fact among the 9 next most stable configurations. Also in this category is the predicted, sought-after positional isomer 1,2,3,9,10,12-Ag_6Au_7 which was subsequently found in the Pt-centered Ag_6Au_6 core of the trimetallic cluster $(Ph_3P)_6Au_6Ag_6Pt(AgI_3)_2$.[36] The utilization

---

(32) See Figure 4 of ref 17b.

(33) (a) Teo, B. K.; Shi, X.; Zhang, H. *J. Am. Chem. Soc.* **1991**, *113*, 4329. (b) Teo, B. K.; Zhang, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 445. (c) Teo, B. K.; Shi, X.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1195. (d) Teo, B. K.; Zhang, H. *Inorg. Chem.* **1991**, *30*, 3115.

(34) (a) Teo, B. K.; Shi, X.; Zhang, H. *Inorg. Chem.* **1993**, *32*, 3987. (b) Teo, B. K.; Zhang, H.; Shi, X. *J. Am. Chem. Soc.* **1990**, *112*, 8552.

(35) Teo, B. K. Unpublished results.

(36) Teo, B. K.; Zhang, H. *J. Organanomet. Chem.* **2000**, *614−615*, 66−69.

Table 8. Most Stable Positional Isomers of $\square_n B_{13-n}$ Clusters Where □ Represents Vacancy

cluster	N_{BB}
1-$\square B_{12}$	36
1,2-$\square_2 B_{11}$	31
1,2,3-$\square_3 B_{10}$	27
1,2,3,4-$\square_4 B_9$	23
1,2,3,4,5-$\square_5 B_8$	19
1,2,3,4,5,6-$\square_6 B_7$	16
1,2,3,4,5,13-$B_6 \square_7$	12
1,2,3,4,13-$B_5 \square_8$	9
1,2,3,13-$B_4 \square_9$	6
1,2,13-$B_3 \square_{10}$	3
1,13-$B_2 \square_{11}$	1

of the most stable icosahedral positional isomers as the building blocks for these vertex-sharing polyicosahedral clusters (cf. Figure 8 for s_n ($n = 1-4$) of ref 18) signifies the energetic control by the “progressive growth” of this particular “cluster of clusters” sequence.

Big-Hole Rule: The Vacancy Effect. In addition to the previously mentioned two rules, a third rule can be deduced from the TBAM calculations. It may be termed the “big-hole” rule because, if A represents vacancies and B designates real atoms, the most stable structures are the ones with the smallest number of fragment(s) of vacancies, or equivalently, the vacancies form the largest sized hole on the surface of the incomplete icosahedron. This is because, when A represents vacancies, all A−A as well as A−B bonds disappear, and the stability of the cluster is determined solely by the number of B−B bonds. As can be seen from Table 3, the largest holes are formed with the one-fragment positional isomer for each of the icosahedral A_nB_{13-n} clusters which turns out to be the most stable configuration because it has the largest number of B−B bonds. Table 8 lists the most stable positional isomers of incomplete icosahedral A_nB_{13-n} clusters and the number of B−B bonds. In this table, the vacancies are represented by □. To assess the relative stabilities of other positional isomers of a given A_nB_{13-n} cluster, one needs only to focus on the numbers of B−B bonds in Table 3 where A is taken to be the vacancies.

We shall illustrate the validity and utility of this third rule with gold-rich clusters. It is known that many high-nuclearity gold-containing clusters are icosahedral-based and can be described as incomplete icosahedra. As is evident from Figure 2 and Table 2 of ref 17b, with only one exception (c(12), the *nido*-icosahedral structure), all c(*n*) primary clusters have been found in gold-containing clusters. Here, $n = 4-13$ represents the nuclearity of an incomplete centered icosahedral cluster. An example of an incomplete icosahedral cluster, c(10), can be found in Figure 3 of ref 17b which is the structure of a decanuclear trimetallic cluster, $(Ph_3P)_7Au_6Ag_3PtCl_3$.[37] The metal core Au_6Ag_3Pt can be described as a Pt-centered icosahedron with 3 vacancies. The 3 vacancies form a triangle which is the largest hole on the surface of the incomplete icosahedron. If we consider the vacancies as virtual atoms of the A type and the metals, be it Au, Ag, or Pt, as real atoms of the B type, then the incomplete icosahedral metal core of the cluster can be described as 1,2,3-A_3B_{10}. An examination of Table 3 revealed that the 5 positional isomers of an incomplete icosahedral A_3B_{10} cluster, 1,2,3-A_3B_{10}, 1,2,4-A_3B_{10}, 1,2,8-A_3B_{10}, 1,2,9-A_3B_{10}, and 1,7,9-A_3B_{10} , have 27, 26, 25, 25, and 24 B−B bonds, with decreasing order of stability. It should be mentioned that, of the first 2 configurations which both have one fragment of vacancies, the “hole” in 1,2,3-A_3B_{10} is the biggest (hence the most stable) because it has a triangular shape while that in 1,2,4-A_3B_{10} is the next biggest (the next most stable) because it has a V shape. The next 2 configurations, 1,2,8-A_3B_{10} and 1,2,9-A_3B_{10}, are two-fragment structures. They have the same energy in the spirit of the tight-binding approach (and hence rank third in stability). Finally, the last configuration 1,7,9-A_3B_{10} is a three-fragment structure which is the least stable.

Conclusion

We believe that the TBAM approach provides a simple and efficient method for assessing the relative energetics or stabilities of various positional isomers of a heteronuclear cluster of a given geometry. It is particularly useful for multicomponent heteronuclear clusters of increasing nuclearity and complexity in structures wherein the number of positional isomers is so large that energy optimization of all possible configurations is impossible.

The fact that the total bond energies exhibit a stepwise progression suggests that positional isomers of a given cluster geometry are characterized, and hence can be categorized, by the numbers of A−A, B−B, and A−B bonds, or simply the numbers of the minority (either A−A or B−B) bonds. Three site preference rules, the strong-bond rule, the heterobond rule, and the big-hole rule, were formulated on the basis of the model calculations. These rules are useful in rationalizing and/or predicting the relative stabilities of various positional isomers of a given cluster geometry.

Acknowledgment. We thank the National Science Foundation for support of this work.

Appendix

Table 9 contains paramaters used in the calculations throughout this paper.

Table 9. Parameters Used in the Calculations

atom	bond energy (kJ/mol)	Pauling’s electronegativity
B	293.00	2.04
C	345.60	2.55
N	247.00	3.04
S	226.00	2.58
Au	61.38	2.54
Ag	47.49	1.93
Ni	71.67	1.91
Pt	94.27	2.28

Supporting Information Available: Tables listing calculated total bond energies (kJ/mol) of all possible positional isomers of B-centered (Table S1) and A-centered (Table S2) binary (A−B = Ag−Au, Ni−Au, and Pt−Au) icosahedral A_nB_{13-n} clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020325B

---

[37] Teo, B. K. To be published.