two redox centers is occupied by solvent molecules, whereas in the trans trimer the solvent is kept away from this region by the bulky linear pz–Ru$(NH_3)_4$–pz "bridge". It is conceivable that the solvent molecules in this critical intersite region of the cis complexes will experience a substantial reorganization upon electron transfer, a contribution to the overall reorganizational energy that is not present in the case of the trans trimer.

**Photophysical Behavior.** As previously observed for the pentaammine systems [2,2,2], [3,2,2], and [3,2,3],[17] the tetraamminepyridine systems investigated in this study ([2′,2,2′], [2′,2,2], [3′,2,3′], [3′,2,3], [2′,2,3′], and [2′,2,3]) do not emit. Although for the oxidized and semioxidized forms perturbation of the d–$\pi^*$ triplet of the Ru$(bpy)_2$ chromophore by the paramagnetic Ru(III) centers could be a possibility, the most likely explanation for the general lack of d–$\pi^*$ emission is radiationless deactivation via low-lying "remote" d–$\pi^*$ (tpye c and d) or IT (type e and f) states. Deactivation schemes for such processes are similar to those previously reported for the pentaammine systems.[17]

An intriguing, new possibility that is specific to the semioxidized mixed pentaammine–tetraammine–pyridine complex [2′,2,3] is depicted in Scheme I. In this scheme, processes 2 + 5 and 1 + 4 represent the possible deactivation pathways of the Ru$(bpy)_2$ d–$\pi^*$ excited state via the "remote" d–$\pi^*$ and IT states, respectively. These pathways are common to all the other trinuclear complexes of the series. For this complex, however, an additional possibility is that secondary hole-transfer (process 6) or electron-transfer (process 7) steps convert these intermediate states to the end-to-end IT state. This deactivation scheme is reminiscent of the intramolecular electron transfer sequence involved in photoinduced charge separation in organic molecular triads.[19-22] The end-to-end IT state has the reduced and oxidized sites separated by two bridging groups and a central chromophore, and can thus be considered analogous to the charge-separated state of the organic triads.

The end-to-end IT state should be readily observable by spectroscopic means, based on the shift in the visible IT band with respect to the ground state (see, for comparison, the spectra of the [3,2,3] and [3′,2,3′] species). The experimental lack of any observable signal in the laser flash photolysis of the [2′,2,3] must be due either to inefficient population or to the short lifetime of the charge-separated, end-to-end IT state. While the latter explanation may be plausible (calculations using the Hush model and the available spectroscopic information give expected lifetimes for this state in the 0.5–2-ns range), the most likely hypothesis seems to be that of inefficient population of the state. As a matter of fact, if process 4 is compared with process 6, the two processes are virtually identical as far as the electronic factors and the intrinsic barriers are concerned, while the former has a more favorable driving force. As both processes are only moderately exergonic and thus likely to lie in the "normal" free energy region of the Marcus theory,[48] the former is also expected to be the fastest one. Similar arguments can be made if process 5 and process 7 are compared.

**Registry No.** [2,2], 94499-30-6; [3,2]$(PF_6)_3$, 94499-27-1; [3,3], 111557-17-6; [2′,2], 111557-19-8; [3′,2]$(PF_6)_3$, 111557-12-1; [3′,3], 111557-18-7; [2,2,2], 94499-29-3; [3,2,2], 94499-28-2; [3,2,3]$(PF_6)_6$, 94499-25-9; [2′,2,2], 111557-22-3; [2′,2,3], 111557-21-2; [3′,2,3]$(PF_6)_6$, 111557-16-5; [3′,3,3], 111557-20-1; [2′,2,2′], 111557-25-6; [2′,2,3′], 111557-24-5; [3′,2,3′]$(PF_6)_6$, 111557-14-3; [3′,3,3′], 111557-23-4; *trans*-[Ru$(NH_3)_4(SO_4)$py]Cl, 63251-18-3; *cis*-Ru$(bpy)_2(CN)_2$, 20506-36-9; [Ru$(NH_3)_5$Cl]$Cl_2$, 18532-87-1.

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Contribution from the Department of Chemistry,
University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680

# Magic Numbers in Atom and Electron Counting of Supraclusters Based on Vertex-Sharing Icosahedra

Boon K. Teo* and Hong Zhang

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The concept of cluster of clusters ($C^2$) is described. In particular, we consider the series of supraclusters based on vertex sharing of centered icosahedra. General formulas for magic numbers in atom and electron counting are given along with examples and predictions. Possible synthetic approaches are suggested. It is hoped that the present results and the methodology illustrated will provide a rational pathway to large metal clusters of increasing nuclearity formed via vertex, edge, or face sharing of smaller cluster units as building blocks.

## Introduction

High-nuclearity gold phosphine clusters are often based on centered 13-atom icosahedral units (Figure 1a).[1] Recently, we reported the structure of a 25-atom cluster containing 13 Au and 12 Ag atoms: viz., $[(Ph_3P)_{10}Au_{13}Ag_{12}Br_8]^+$ (**1**).[2a] Its metal framework (Figure 1b) can be considered as two Au-centered $Au_7Ag_6$ icosahedra sharing one vertex (nuclearity = 2 × 13 − 1 = 25). We also succeeded in isolating and structurally characterizing a new type of 38-atom cluster, $[(R_3P)_{12}Au_{18}Ag_{20}Cl_{14}]$ (**2**) (where R = $p$-$MeC_6H_4$).[3a] This cluster can be visualized as three Au-centered $Au_7Ag_6$ icosahedra sharing three corners in a triangular arrangement, which gives rise to a hypothetical 36-atom cluster (Figure 1c); the linkage of two additional exopolyhedral Ag atoms to the top and the bottom $Ag_3$ triangles along the threefold axis results in the observed 38-atom cluster (**2**).

The most interesting structural characteristic of these two clusters is that both can be considered as being built up from smaller cluster units by vertex sharing. This opens up new pathways to larger metal clusters via fusion of smaller cluster units as building blocks. We refer to this particular oligomerization

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(1) For reviews of gold phosphine clusters, see, e.g.: (a) Steggerda, J. J.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 164. (b) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1985**, 237–325. (c) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: 1978.

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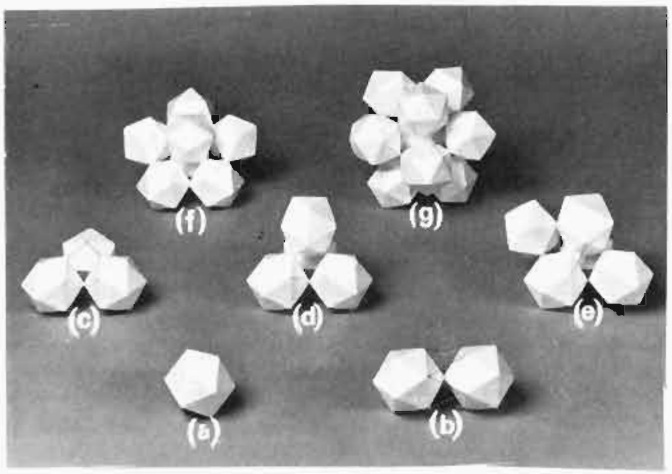

**Figure 1.** Supracluster $s_n$ formed by *n* vertex-sharing centered icosahedra (nuclearity in parentheses): (a) $s_1(13)$; (b) $s_2(25)$; (c) $s_3(36)$; (d) $s_4(46)$; (e) $s_5(56)$; (f) $s_7(76)$; (g) $s_{12}(127)$.

concept as *cluster of clusters* and to the resulting clusters as *supraclusters*.

Understanding the atomic arrangements and the electronic requirements of these supraclusters is a prerequisite to the design and synthesis of metal clusters of increasing nuclearity.[4,5] We wish to explore here the *magic numbers*[6] in atom and electron counting of supraclusters ($s_n$) formed by *n* vertex-sharing icosahedral cluster units of 13 atoms each. We have discovered some remarkably simple general formulas for these magic numbers that not only yield valuable information concerning possible molecular architectures (i.e., the number and disposition of atoms within each cluster) but also provide new insight regarding the bonding of this particular cluster series. These atom- and electron-counting results enable one to rationalize the stereochemistry and ligand requirements for the known members as well as to predict the geometrical features for the (as yet) unknown members.

Parts a–g of Figure 1 depict the series of metal supraclusters ($s_n$) formed by *n* vertex-sharing centered 13-atom icosahedra, where $n$ = 1, 2, 3, 4, 5, 7, and 12, respectively. Other *n* values are not likely to occur on the basis of stereochemical considerations. To date, only the first three members (or their close relatives) of the series have been synthesized and structurally characterized. We shall discuss in some detail these known clusters and then generalize to predict the electron count of the others.

## Cluster of Clusters ($C^2$) Model

According to the cluster of clusters ($C^2$) model, for a supracluster formed by *n* polyhedral clusters, the number of shell (skeletal) electron pairs, *B*, is given by the sum of the individual $B_j$ values ($j = 1-n$) *minus* the sum of the $B_k$ values ($k = 1-s$) of the *s*-shared vertices, edge(s), or face(s):

$$B = \sum_j^n B_j - \sum_k^s B_k \tag{1}$$

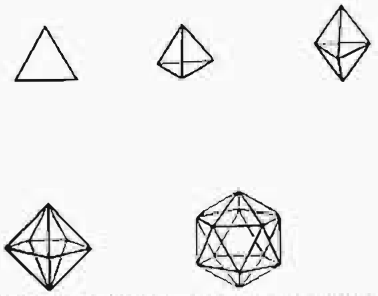

**Figure 2.** Superdeltahedra formed by centroids of *n* vertex-sharing icosahedral units where $n$ = 3 (triangle), 4 (tetrahedron), 5 (trigonal bipyramid), 7 (pentagonal bipyramid), and 12 (icosahedron). See text.

Equation 1 is based on the assumption that the overall *B* value is the sum of the $B_j$ values of the individual *n* building blocks *minus* the sum of the $B_k$ values of the shared *s* components (to avoid overcounts). For example, the $B_k$ values for sharing a vertex, an edge, a triangle, a square, a pentagon, and a hexagon are 3, 5, 6, 8, 10, and 12, respectively.[7-9]

According to the topological electron counting (TEC) rule,[7-9] the total number of valence electron pairs in a given polyhedral arrangement is given by

$$T = V_n + 6V_m + B \tag{2}$$

where *V* is the total number of vertices (i.e., $V = V_n + V_m$, where $V_n$ and $V_m$ represent the number of noninterstitial main-group and noninterstitial (i.e., surface) transition-metal atoms, respectively). The total valence electron count is $N = 2T$.

For the 25-atom cluster formed by *two* icosahedra sharing *one* vertex (cf. Figure 1b, eq 1 predicts $B = 2 \times 13$ (icosahedron) $- (1 \times 3)$ (sharing one vertex) = 23, while eq 2 predicts $T = 6V_m + B = 6 \times (25 - 2) + 23 = 161$ skeletal electron pairs or a total valence electron count of $N = 2 \times 161 = 322$. One known example is the $[(Ph_3P)_{10}Au_{13}Ag_{12}Br_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_4]^+$ cluster (**1**) for which the $N_{obsd}$ of $(10 \times 2 + 25 \times 11 + 2 \times 1 + 2 \times 3 + 4 \times 5 - 1) = 322$ valence electrons is in accordance with the calculated value. Likewise, *three* 13-atom icosahedra (Figure 1c) sharing *three* vertices in a cyclic manner results in $B = (3 \times 13) - (3 \times 3) = 30$ (eq 1). For such a 36-metal atom cluster, $T = 6V_m + B = 6 \times (36 - 3) + 30 = 228$ (eq 2) and $N = 2 \times 228 = 456$. This cluster is presently unknown. However, the closely related 38-metal atom cluster $[(R_3P)_{12}Au_{18}Ag_{20}Cl_{14}]$ (where R = $p$-$MeC_6H_4$) is predicted to have $456 + 2 \times 18 = 492$ valence electrons if the two exopolyhedral Ag atoms do not form metal–metal bonds with the 36-atom polyhedral framework, as is indeed observed ($N_{obsd} = 12 \times 2 + 38 \times 11 + 2 \times 1 + 6 \times 3 + 6 \times 5 = 492$). However, if six metal–metal bonds (three on each side) are formed between the two exopolyhedral Ag atoms and the polyhedral atom framework, the electron count would be $492 - 12 = 480$.

## Magic Numbers: Atom Counting

We shall now provide a generalization of the above *atom*- and *electron*-counting results for supraclusters ($s_n$) formed by *n* vertex-sharing centered icosahedra arranged in a nearly close-packed manner (cf. Figure 1). Here we assume the *centers* of the icosahedral units form a "superpolyhedron" (cf. Figure 2) with *n* vertices, *e* edges, and *f* faces.

We further assume that the shared vertices reside on the midpoints of the edges of the superpolyhedron. Since there are 13 atoms per centered icosahedral unit, the nuclearity $G_n$ of the supracluster $s_n$ is given by 13*n* *minus* the number of shared vertices, which is equal to be number of edges (*e*) of the superpolyhedron:

$$G_n = 13n - e \tag{3}$$

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(4) (a) Ozin, G. A.; Mitchell, S. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 674. (b) Messmer, R. P.; Knudson, S. K.; Johnson, K. H.; Diamond, J. B.; Yang, C. Y. *Phys. Rev. B: Solid State* **1976**, *13*, 1396. (c) Yang, C. Y.; Johnson, K. H.; Salahub, D. R.; Kaspar, J.; Messmer, R. P. *Phys. Rev. B: Condens. Matter* **1981**, *24*, 5673. (d) Hoare, M. R.; Pal, P. *Adv. Phys.* **1971**, *20*, 161. (e) Burton, J. J. *Catal. Rev.—Sci. Eng.* **1974**, *9*, 209. (f) Hoare, M. R.; Pal, P. *Adv. Phys.* **1975**, *24*, 645. (g) Hoare, M. R. *Adv. Chem. Phys.* **1979**, *40*, 48. (h) Hoare, M. R.; Pal, P. *Nature (London) Phys. Sci.* **1972**, *236*, 35. (i) Hoare, M. R.; Pal, P. *Nature (London)* **1971**, *230*, 5. (j) Burton, J. J. *Chem. Phys. Lett.* **1970**, *3*, 594. (k) Burton, J. J. *Nature (London)* **1971**, *229*, 335. (l) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

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(8) Teo, B. K. *Inorg. Chem.* **1985**, *24*, 1627.

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For example, triangular (of $D_{3h}$ symmetry), tetrahedral ($T_d$), trigonal-bipyramidal ($D_{3h}$), pentagonal-bipyramidal ($D_{5h}$), and icosahedral ($I_h$) arrays of vertex-sharing icosahedra, which have 3, 6, 9, 15, and 30 shared vertices, respectively, will give rise to corresponding nuclearities of $3 \times 13 - 3 = 36$, $4 \times 13 - 6 = 46$, $5 \times 13 - 9 = 56$, $7 \times 13 - 15 = 76$, and $12 \times 13 - 30 = 126$ atom clusters (as depicted in Figure 1d–g). In fact, for a superdeltahedron (i.e., a polyhedron with only triangular faces) with $n$ ($>3$) vertices, the number of edges is given by

$$e = 3n - 6 \tag{4}$$

and the number of faces by

$$f = 2n - 4 \tag{5}$$

Combining eq 3 and 4, we obtain a general formula for the nuclearity ($n > 3$) for a deltahedral supracluster:

$$G_n = 13n - (3n - 6) = 10n + 6 \tag{6}$$

For example, $G_n = 36$, 46, 56, 76, and 126 for $n = 3$, 4, 5, 7, and 12, respectively, as previously derived. The icosahedral supracluster of $I_h$ symmetry formed by 12 centered icosahedra sharing 30 corners deserves some comments. Here the icosahedral hole created by the 12 icosahedra can be filled with one additional atom resulting in the nuclearity of $G_{12} = 12 \times 13 - 30 + 1 = 127$.

The number of surface atoms (including the shared vertices) is

$$S_n = (10n + 6) - n = 9n + 6 \tag{7}$$

We can further define the Au/Ag composition in the supraclusters if we assume that it is formed by *Au-centered* $Au_7Ag_6$ icosahedra sharing *Au vertices*. Hence, the number of Au atoms is $7n - e = 7n - (3n - 6) = 4n + 6$, while the number of Ag atoms is $6n$; the resulting formulation is $Au_{4n+6}Ag_{6n}$. Judging from the triangular series of $M_{36}$ and $M_{38}$ clusters, we can reasonably expect that each supracluster with $n$ icosahedral units may develop into a series of $M_{10n+6+m}$ supraclusters (e.g., $Au_{4n+6}Ag_{6n+m}$) where $m = 0$ to $(2n - 4)$ is the number of exopolyhedral metal atoms capping the $(2n - 4)$ triangular faces of the superdeltahedron. For example, the tetrahedral supracluster may include a five-membered series of $M_{46+m}$ where $m = 0$–4 is the number of metal atoms (most likely Ag for the AuAg system) capping the four triangular faces of the supertetrahedron.

There are, of course, many ways in which supraclusters can be formed by vertex sharing of centered icosahedra. We consider here only those in which the centers of the icosahedra form a superdeltahedron of high symmetry (cf. Figure 2). Other arrangements (for example, a linear array) are also possible. The methodology presented here can easily be extended to other systems.

## Magic Numbers: Electron Counting

Given the above atom-counting results, we can calculate the number of shell (skeletal) electron pairs as follows. Since each icosahedral unit contributes 13 electron pairs and each shared vertex (total number = $e$) diminishes the $B$ value by 3, the use of eq 1 and 4 gives rise to the $B_n$ value for a supracluster $s_n$ being

$$B_n = 13n - 3e = 13n - 3(3n - 6) = 4n + 18 \tag{8}$$

Combining eq 7 and 8 gives the total number of electron pairs as

$$T_n = 6S_n + B_n = 6(9n + 6) + (4n + 18) = 58n + 54 \tag{9}$$

and the total electron count is

$$N_n = 2T_n = 116n + 108 \tag{10}$$

Thus, the trigonal ($D_{3h}$), tetrahedral ($T_d$), trigonal-bipyramidal ($D_{3h}$), pentagonal-bipyramidal ($D_{5h}$), and icosahedral ($I_h$) supraclusters $s_n$ are predicted to have $B_n = 30$, 34, 38, 46, and 66, in steps of 4 for each increment of $n$, and $T_n = 228$, 286, 344, 460, and 750, in steps of 58 for each increment of $n$, respectively. The corresponding electron counts are 456, 572, 688, 920, and 1500, in steps of 116 for each increment of $n$.

There are, of course, numerous formulas that satisfy the electron counts predicted by eq 10: for example, the series $[L_lM_mX_p(\mu\text{-}X)_r(\mu_3\text{-}X)_t]^{q+}$ requires that $2l + 11m + p + 3r + 5t - q = N_n = 116n + 108$ where L represents a two-electron donor, M a coinage metal, and X a halogen ligand.

Possible examples of the trigonal, tetrahedral, trigonal-bipyramidal, pentagonal-bipyramidal, and icosahedral supraclusters are $L_{12}M_{36}(\mu\text{-}X)_{12}$, $L_{12}M_{46}(\mu\text{-}X)_{14}$, $L_{12}M_{56}(\mu\text{-}X)_{16}$, $L_{12}M_{76}(\mu\text{-}X)_{20}$, and $[L_{12}M_{127}(\mu\text{-}X)_{27}]^{2+}$, respectively (or their charged variants). Note that in this particular series of supraclusters, the metal core, with nuclearities of 36, 46, 56, 76, and 127, is encaged in a more or less spherical arrangement of 12 phosphine ligands.

## Synthetic Strategies

We wish to propose a synthetic approach for the supraclusters ($s_n$) studied here via a stepwise *agglomeration* of smaller cluster units. The feasibility of the idea is based on our recent kinetic study[10] which showed that the 25-atom cluster ($Au_{13}Ag_{12}$) is a precursor of the 38-atom cluster ($Ag_{18}Ag_{20}$).

It is conceivable that the $s_n$ (nuclearity) supraclusters can be formed in a stepwise manner with progressive *reduction* ([R]) as follows (cf. Figure 1):

$$M^{1+} \xrightarrow{[R]} s_1(13) \xrightarrow{[R]} s_2(25) \xrightarrow{[R]} s_3(36) \xrightarrow{[R]}$$
$$s_4(46) \xrightarrow{[R]} s_5(56) \xrightarrow{[R]} s_7(76) \xrightarrow{[R]} s_{12}(127)$$

In fact, the two additional exo-polyhedral Ag atoms in the 38-atom cluster signify the ultimate existence of $s_4(46)$ and $s_5(56)$ supraclusters, as they may serve as center(s) of or *anchors* for the growth of additional icosahedral unit(s).

On the basis of the determined structures of the 13-, 25- and 38-atom clusters and the electron-counting results presented here, we can calculate the "average" formal oxidation state of the metal atoms in the supraclusters as follows (assuming the above-mentioned series of clusters):

$$M^{1+} \xrightarrow{[R]} s_1^{0.38+} \xrightarrow{[R]} s_2^{0.36+} \xrightarrow{[R]} s_3^{0.33+} \rightarrow s_4^{0.30+} \xrightarrow{[R]}$$
$$s_5^{0.28+} \xrightarrow{[R]} s_7^{0.26+} \xrightarrow{[R]} s_{12}^{0.23+}$$

It follows that, in order to synthesize higher nuclearity clusters, we must employ a larger amount of and/or a stronger reducing agent. This is analogous, albeit in opposite direction, to the preparation of high nuclearity one-dimensional triangular platinum (or nickel) carbonyl dianions via successive *oxidations* ([O]):[11]

$$(Pt_3)^{0.67-} \xrightarrow{[O]} (Pt_3)_2^{0.33-} \xrightarrow{[O]} (Pt_3)_3^{0.22-} \xrightarrow{[O]} (Pt_3)_4^{0.17-} \xrightarrow{[O]}$$
$$(Pt_3)_5^{0.13-} \xrightarrow{[O]} (Pt_3)_6^{0.11-} \rightarrow \ldots$$

where $(Pt_3)_n$ represents a stack of $n$ $Pt_3(CO)_6$ units. Within the series, the smaller the magnitude of the formal oxidation state, the larger will be the cluster.

## Nearly Close Packing of Metal Atoms

It should be emphasized that the vertex-sharing icosahedral supraclusters discussed here are based on nearly (but not exactly) close packing of metal atoms. The metal–metal distances *between* the icosahedral units are somewhat longer than the metal–metal distances *within* the units.

For example, Figure 3 depicts the metal framework of the predicted, yet unknown, 36-atom cluster (Figure 1c). Imagine a two-dimensional close packing of 12 Au atoms forming a $\nu_2$ triangle and three $\nu_1$ triangles sharing corners. Above and below the three small triangles are six Au atoms, conceptually changing the smaller triangles into trigonal bipyramids. Above and below the central (large) triangle are three Ag atoms each arranged in

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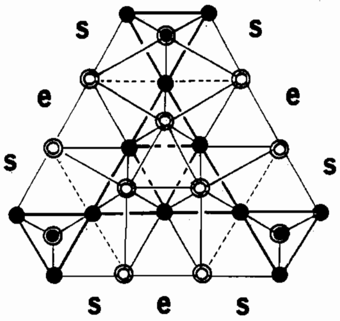

**Figure 3.** Schematic representation illustrating the nearly close packing of the metal framework of the proposed 36-atom cluster $L_{12}Au_{18}Ag_{18}X_{12}$ where L is a phosphine ligand and X is a doubly bridging halogen ligand. The filled and open circles represent Au and Ag atoms, respectively.

a truncated $\nu_2$ tetrahedral array. On the three edges are 12 Ag atoms (*not closest packed*), six above and six below the plane of the 12 Au atoms. This observation is in accord with the extended Hume–Rothery rule,[12] which predicts that the number of electrons per (bulk) metal atoms is somewhat greater than that expected for closest icosahedral (11.17) or face-centered-cubic (11.24) packing.

## Conclusion

The newly developed $C^2$ model, in combination with the TEC approach, can provide new insight into molecular and electronic requirements of larger supraclusters based on smaller cluster units. Here we consider the series of supraclusters based on vertex sharing of centered icosahedra. General formulas for magic numbers in atom and electron counting are given along with examples and predictions. Possible synthetic approaches are suggested. It is hoped that the present results and the methodology illustrated will provide a rational pathway to obtain large metal clusters of increasing nuclearity (formed via vertex, edge, or face sharing of smaller cluster units as building blocks).

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