Tri- and Tetra-superatomic Molecules in Ligand-Protected Face-Fused Icosahedral (M@Au12)n (M = Au, Pt, Ir, and Os, and n = 3 and 4) Clusters

Chang Xu, † Yichun Zhou, † Jiuqi Yi, Dan Li, Lili Shi, and Longjiu Cheng*

ABSTRACT: Cluster assembling has been one of the hottest topics in nanochemistry. In certain ligand-protected gold clusters, bi-icosahedral cores assembled from Au13 superatoms were found to be analogues of diatomic molecules F2, N2, and singlet O2, respectively, in electronic shells, depending upon the super valence bond (SVB) model. However, challenges still remain for extending the scale in cluster assembling via the SVB model. In this work, ligand-protected tri- and tetra-superatomic clusters composed of icosahedral M@Au12 (M = Au, Pt, Ir, and Os) units are theoretically predicted. These clusters are stable with reasonable highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gaps and proven to be analogues of simple triciatomic (ClO−, OCl2, O3, and CO2) and tetra-atomic (N≡C–C≡N, and Cl–C≡C–Cl) molecules in both geometric and electronic structures. Moreover, a stable cluster-assembling gold nanowire is predicted following the same rules. This work provides effective electronic rules for cluster assembling on a larger scale and gives references for their experimental synthesis.

Ligand-protected gold clusters have been intensively studied during the past decades as a result of their intriguing properties and wide potential applications.1−12 Certain gold clusters are described as superatoms (SAs), because electron shell configurations of their Au cores follow the Jellium model, in which valence electrons fill discrete superatomic orbitals (1s21p6) and icosahedral geometry. The central atom in icosahedral Au13 can be replaced by other metal atoms to regulate the number of their valence electrons,29 and these icosahedrons are rational building blocks for cluster assembling.36−44

A number of assemblies composed of all-gold icosahedrons or monometallic-doped icosahedrons have been obtained, in which the icosahedral units are linked through ligands, interatomic bonds, or van der Waals interactions conventionally.42−50 The super valence bond (SVB) model proposed by our group51−53 gives the new perspective for the electronic shell of superatomic clusters, which points out that superatoms can form superatomic molecules through the SVB by sharing nuclei and valence electrons. On the basis of the SVB model, the bi-icosahedral cores in [Au68(SR)34]Cl2,52 [Au38(SR)24]53,54 [Au22(dppo)6]55 and Au22H4(dppo)6 clusters are proven to be bi-superatomic molecules with super single, triple, and quadruple bonds through density functional theory (DFT) calculations, which can be considered as analogues of diatomic molecules, such as F2, N2, and Re2.57 Beside the linear structure, SVBs are also observed in some three-dimensional arrays, including [Au6{Ni3(CO)6}4]42− and Au70S20(PPh3)12, reported by Muñoz-Castro.58,59 Moreover, a series of clusters formed by two icosahedral M@Au12 (M = Pd and Pt) superatoms are theoretically designed on the basis of the SVB model and targetedly synthesized by Tsukuda et al.,60 of which one has an electronic configuration similar to that of singlet O2. The bond orders of SVBs in M4Au16(SR)24 (M = Au, Pd, and Pt) clusters can be reversibly controlled by tuning their charge states, to obtain the single-, double-, and triple-bonded superatomic molecules.61

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The SVB model reveals the bonding rule between two homogeneous superatoms, which provide another possible pattern for cluster assembly, that is, assembling superatoms in the same way as atoms. Thus far, a number of bi-superatomic molecules are designed following the SVB model, but further development is still needed to reveal the possibility for superatom assembling on a larger scale based on the same rule.

In this paper, efforts are made to extend the superatomic framework to tri- and tetra-superatomic molecules through the SVB model. The ligand-protected tri- and tetra-icosahedron clusters formed by face-sharing M@Au12 (M = Au, Pt, Ir, and Os) superatomic icosahedrons are designed. In each M@Au12 superatomic molecule, Cl3 and O, N, and C atoms with seven, six, and four valence electrons, respectively. Therefore, these tri- and tetra-superatomic molecules are proven to be electronic analogues.

The electronic shell closure is obtained through super valence bonds. Because different atomic dopants provide different numbers of valence electrons in the Jellium potential, the series of metal-doped [M = Au, Pt, Ir, and Os] superatomic icosahedrons are designed. In each M@Au12 icosahedral superatom, 12 Au atoms on the surface are either protected by staple motifs or shared with other superatoms, and thus, each atom contributes 0.5 valence electrons to the superatomic shell (6e in total). Because different atomic dopants provide different numbers of valence electrons in the Jellium potential, the series of metal-doped [M = Au, Pt, Ir, and Os] superatomic icosahedrons can be treated as electronic analogues of Cl, O, N, and C atoms with seven, six, and four valence electrons, respectively. Therefore, these tri- and tetra-superatomic molecules are proven to be electronic analogues of Cl−, OCl2, CO2, O3, N≡C−C≡N, and Cl−C≡C−Cl molecules in their bonding frameworks. Following the same rule, a stable superatomic nanowire composed of Pt@Au12 icosahedrons is predicted, as a linear assembling of 6e superatoms, in which the electronic shell closure is obtained through super valence bonds.

Here, geometric structures of these superatom assemblies are built and fully optimized at the PBE0/def2svp level of theory. All structures are verified to be true minima by frequency check. A halogen (Cl) is chosen to replace sulfur (S) for convenience. As shown in Table 1, these clusters have similar geometric symmetries and fairly large electronic shell closure. The electronic shell of the Au33 core in [Au33(Au18Cl30)]+ is almost identical to that of Au25(SR)18. The formulas of these cluster are written as [core(ligand)]ion for convenience. As shown in Table 1, these clusters have similar geometric symmetries and fairly large electronic shell closure.

The geometry of [Au33(Au18Cl30)]+ (1) is formed by face-fused tri-icosahedral Au13 cores, as shown in Figure 1a, of which 24 vertexes are studded by six Au2Cl3 and six AuCl2 oligomers (Figure 1b). It could be viewed as a union of three Au13 icosahedrons, in which a Au3 triangle face is shared by the two adjacent icosahedral units (Figure 1c).

The electronic shell of the Au13 core in [Au33(Au18Cl30)]+ (1) is further discussed. Because each staple motif withdraws one electron, the Au33 core with a tri-icosahedral structure has 22 valence electrons, which is supposed to be an analogue of the Cl− molecule in both electronic and geometric structures. To verify our inference, the bonding pattern of Au33 is investigated using the adaptive natural density partition (AdNDP) method, which is widely used in discussions of localized multicenter chemical bonding. The results reveal that this Au33 core is formed by three open-shell SAs through SVBs. As shown in Figure 2a, there are three 13c−2e super lone pairs (LPS) (super s, pα, and pβ) in each SA. The pα orbital in each SA composes one σ bonding, one σ non-bonding, and one σ antibonding orbitals, and the former two orbitals are occupied as three superatomic center–two electron (3sc−2e) super bonds. As we know, in the Cl− molecule, there are three LPS in each atom and two 3c−2e σ bonds (one σ and one σσ) as shown in Figure 2b. Therefore, this Au33 core is an electronically analogous to Cl− in the bonding framework. Moreover, a comparison of the Kohn–Sham molecular orbitals (MOs) between the [Au33(Au18Cl30)]+ cluster and Cl− molecule also confirms their similarity in electronic shells (Figure S1 of the Supporting Information). This superatomic bonding pattern is different from the [Au37(PPh3)10(SR)10X2]+ cluster, which was theoretically predicted in 2007 and experimentally obtained in 2015. The Au37 core in [Au37(PPh3)10(SR)10X2]+ also shows a rod-like structure composed of three icosahedral Au13 units, but it is assembled through vertex–vertex fusion rather than the face–face pattern.

### Table 1. Symmetries, HOMO–LUMO Energy Gaps (E_{H-L}), Lengths of SVBs (R_{SA-SA}), Number of Valence Electrons for Tri- and Tetra-superatomic Molecules Formed by M@Au12 (M = Au, Pt, Ir, and Os) Icosahedrons, and Their Analogues (PBE0/def2svp)

<table>
<thead>
<tr>
<th>superatomic molecule</th>
<th>symmetry</th>
<th>E_{H-L} (eV)</th>
<th>R_{SA-SA} (Å)</th>
<th>valence electrons</th>
<th>analogue</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Au13(Au18Cl30)]+</td>
<td>S_6</td>
<td>1.39</td>
<td>4.16</td>
<td>22e</td>
<td>Cl−</td>
</tr>
<tr>
<td>[PtAu12(Au18Cl30)]</td>
<td>S_6</td>
<td>1.55</td>
<td>4.30</td>
<td>20e</td>
<td>OCl_2</td>
</tr>
<tr>
<td>[Os2PtAu12(Au18Cl30)]</td>
<td>S_6</td>
<td>0.70</td>
<td>4.30</td>
<td>16e</td>
<td>CO_2</td>
</tr>
<tr>
<td>[PtAu12(Au18Cl30)]</td>
<td>S_6</td>
<td>1.19</td>
<td>4.22</td>
<td>18e</td>
<td>O_3</td>
</tr>
<tr>
<td>[Os2IrAu12(Au18Cl30)]</td>
<td>D_3</td>
<td>1.05</td>
<td>4.52 (3.91)</td>
<td>18e</td>
<td>N≡C−C≡N</td>
</tr>
<tr>
<td>[Os2Au11(Au18Cl30)]</td>
<td>D_3</td>
<td>1.30</td>
<td>3.92 (4.60)</td>
<td>22e</td>
<td>Cl−C≡C−Cl</td>
</tr>
</tbody>
</table>

*R_{SA-SA} is defined as distances between central metals in adjacent superatomic icosahedrons. *bR_{Os-Os} (R_{Os−Os}). *cR_{Os−Os} (R_{Os−Au}).
As shown in Figure S2 of the Supporting Information, each icosahedral Au$_{13}$ is a closed-shell SA ($1s^21p^6$), and they form a stable tri-superatom molecule through the superatom networks without sharing valence electrons.

The PtAu$_{32}$ core in [PtAu$_{32}$(Au$_{18}$Cl$_{30}$)]$^-$ (1) is also formed by three face-sharing icosahedrons, but it has 20 valence electrons, which is two electrons less than the core in [Au$_{33}$(Au$_{18}$Cl$_{30}$)]$^-$ (1), and could be taken into comparison with the linear OCl$_2$ molecule. The tri-superatomic electronic shell of this PtAu$_{32}$ core is confirmed by AdNDP results in Figure 3a. There are three 13c–2e super LPs (super $s$, p$_x$, and p$_y$) in each SA on the sides and two LPs (super p$_x$ and p$_y$) in the middle SA. Two 2sc–2e super $\sigma$ bonds are formed by sp hybrid orbitals of the middle SA and the p$_z$ orbital of two side SAs, to reach the electronic shell closure. It is actually an electronic analogue of the OCl$_2$ molecule with two 2c–2e $\sigma$ bonds formed by sp hybrid orbitals of the O atom and the p$_z$ orbital of the Cl atom (Figure 3b).

The OsPt$_2$Au$_{30}$ core in [OsPt$_2$Au$_{30}$(Au$_{18}$Cl$_{30}$)] (3) has a geometry similar to that of the Au$_{33}$ core composed of three face-fused icosahedrons, but the Au atoms in centers of three Au$_{13}$ cages are replaced by one Os (middle) and two Pt (sides) atoms, respectively, to change the number of valence electrons. This OsPt$_2$Au$_{30}$ core with 16 valence electrons is also supposed to be a tri-superatomic molecule. The AdNDP calculation reveals that there is one super LP (super $s$) in each Pt@Au$_{12}$ icosahedron, and the rest of the 12 valence electrons occupy two 2sc–2e super $\sigma$ bonds, two 3sc–2e super $\pi$ bonds, and two n$\pi$ bonds. Dependent upon the orbital shape, two super $\sigma$ bonds are formed by the sp hybrid orbitals of Os@Au$_{12}$ and the p$_z$ orbitals in Pt@Au$_{12}$ respectively, and other four super $\pi$/n$\pi$ bonds are formed by p$_x$–p$_x$, p$_y$–p$_y$, p$_x$–p$_y$, and p$_y$–p$_x$. 

Figure 2. Structures, AdNDP localized bonds, and electronic occupation numbers (ONs) of the (a) Au$_{13}$ core in tri-superatomic molecule [Au$_{33}$(Au$_{18}$Cl$_{30}$)]$^-$ (1) and (b) Cl$^-$ molecule.

Figure 3. Structures, AdNDP localized bonds, and electronic ONs of the (a) PtAu$_{32}$ core in tri-superatomic molecule [PtAu$_{32}$(Au$_{18}$Cl$_{30}$)] (2) and (b) OCl$_2$ molecule (Au$_{13}$, yellow polyhedron; Pt@Au$_{12}$, green polyhedron).
interactions between three icosahedrons. Therefore, the OsPt$_2$Au$_{30}$ core is composed of one 4e open-shell superatom (Os@Au$_{12}$ with 1s$^2$1p$^2$) and two 6e open-shell superatoms (Pt@Au$_{12}$ with 1s$^2$1p$^4$) through two super double bonds. The molecule-like electronic shell closure of OsPt$_2$Au$_{30}$ is an analogue of the CO$_2$ molecule (Figure 4b).

Figure 4. Structures, AdNDP localized bonds, and electronic ONs of the (a) OsPt$_2$Au$_{30}$ core in tri-superatomic molecule [OsPt$_2$Au$_{30}$Au$_{18}$Cl$_{30}$] (3) and (b) CO$_2$ molecule (Pt@Au$_{12}$, green polyhedron; Os@Au$_{12}$, red polyhedron).

Figure 5. Structures, AdNDP localized bonds, and electronic ONs of the (a) Pt$_3$Au$_{30}$ core in tri-superatomic molecule [Pt$_3$Au$_{30}$Au$_{18}$Cl$_{30}$] (4) and (b) linear O$_3$ molecule.
Then, we use the Pt atom to replace the Os atom in the center of \([\text{OsPt}_2\text{Au}_{39}(\text{Au}_{21}\text{Cl}_{36})](D_3)\) (3), to obtain a superatomic analogue of the linear \(O_3\) molecule. The \(\text{Pt}_3\text{Au}_{30}\) core of the \([\text{Pt}_3\text{Au}_{10}(\text{Au}_{18}\text{Cl}_{30})]\) (4) cluster has 18 electrons, in which each \(\text{Pt}\)@\(\text{Au}_{12}\) icosahedron has 6 valence electrons and could be viewed as open-shell SAs (1s\(^2\)1p\(^6\)) depending upon the AdNDP analysis. As shown in Figure 5a, there are two 13c\(\rightarrow\)2e super LPs (super s and p\(_x\)) in each \(\text{Pt}\)@\(\text{Au}_{12}\) SA on the side and one 13c\(\rightarrow\)2e super LP (super p\(_x\)) in central \(\text{Pt}\)@\(\text{Au}_{12}\) SA. The molecule-like electronic shell closure of \(\text{Pt}_3\text{Au}_{30}\) is achieved through two 2sc\(\rightarrow\)2e super \(\sigma\) bonds and two 2sc\(\rightarrow\)2e super \(\pi\) bonds, similar to that of the linear \(O_3\) molecule.

![Figure 6](https://example.com/fig6.png)

**Figure 6.** Structures, AdNDP localized bonds, and electronic ONs of the (a) \(\text{OsIr}_2\text{Au}_{39}\) core in tetra-superatomic molecule \([\text{OsIr}_2\text{Au}_{39}(\text{Au}_{21}\text{Cl}_{36})]\) (5) and (b) \(\text{N}≡\text{C}≡\text{C}≡\text{N}\) molecule (\(\text{Ir}\)@\(\text{Au}_{12}\), green polyhedron; \(\text{Os}\)@\(\text{Au}_{12}\), red polyhedron).

![Figure 7](https://example.com/fig7.png)

**Figure 7.** Structures, AdNDP localized bonds, and electronic ONs of the (a) \(\text{Os}_2\text{Au}_{41}\) core in tetra-superatomic molecule \([\text{Os}_2\text{Au}_{41}(\text{Au}_{21}\text{Cl}_{36})]\) cluster (6) and (b) \(\text{Cl}≡\text{C}≡\text{Cl}\) molecule (\(\text{Au}_{13}\), yellow polyhedron; \(\text{OsAu}_{12}\), red polyhedron).
which is in accordance with the electronic shell of the Nf
Au13 icosahedron, three 2sc
AdNDP analysis con
between two Os atoms and 3.91 Å between adjacent Ir and Os
between adjacent icosahedral cages are di
valence electrons in this tetra-icosahedral core, and the lengths
the middle and Ir on the sides) icosahedrons. There are 18
bonds in the Os 2Au41 core, and the superatomic bonding
hybrid orbitals (in each Os@Au12 SA) and four double-
sp2 hybridization.
V-shaped, as the atomic orbitals in the central O atom undergo
shell of Os2Au41 would be similar to that of the Cl
and 4.60 Å, respectively; thus, we suppose that the electronic
between two Os atoms and adjacent Au and Os atoms are 3.92
Thus, it is supposed to be a tetra-superatomic molecule similar
to N≡C–C≡N with interval single and triple bonds. AdNDP
analysis confirms this inference. As shown in Figure 6a, there is one 13c−2e super LP (super s) in each Ir@Au12
SA, and the seven 2sc−2e super bonds consisted of three σ-
bonding orbitals formed by pz (in each Ir@Au12 SA) and sp
hybrid orbitals (in each Os@Au12 SA) and four double-degenerate π bonds composed of px−pz and px−py interactions
(in Ir@Au12 and Os@Au12 SAs). Therefore, there is one super single bond and two super triple bonds in the Os3Ir3Au19 core, which is in accordance with the electronic shell of the N≡C–
C≡N molecule, as shown in Figure 6b.
The Os2Au41 core of the [Os2Au41(Au21Cl36)] cluster (6) has a geometric structure similar to that of Ir2Os2Au39, but the electronic shells are different because two Ir atoms in
Ir2Os2Au39 are substituted by two Au atoms. The lengths between two Os atoms and adjacent Au and Os atoms are 3.92
and 4.60 Å, respectively; thus, we suppose that the electronic shell of Os2Au41 would be similar to that of the Cl–C≡C–Cl
molecule. AdNDP results in Figure 7a reveal that there are three 13c−2e super LPs (super s, pσ, and pπ) localized in each
Au41 icosahedron, three 2sc−2e super σ bonds formed by pσ
(in each Au41 SA) and sp hybrid orbitals (in each Os6@Au41
SA), and two 2sc−2e π bonds composed of double-degenerate π bonds of pπ−pz and pπ−py (in each Os6@Au41 SA).
Therefore, there is one super triple bond and two super single bonds in the Os6@Au41 core, and the superatomic bonding
framework (3σ2π) is a nice analogue of the Cl–C≡C–Cl molecule.

Lengths of the super bonds also present important evidence
for the superatomic bonding characters in these tetra-
superatomic molecules. All of the superatomic molecules are composed of the icosahedral M@Au12 cage, and the super
bond length is defined as the distance between central metals in
adjacent superatoms (as shown in Table 1). For
[Os2Ir2Au39(Au21Cl36)], the super single bond length (R Os–Os
= 4.52 Å) is obviously larger than the super triple bond (R Os–Os
= 3.91 Å), which is in accordance with its bonding characters.
The super bond lengths in [Os2Au41(Au21Cl36)] also confirm its bonding pattern, in which the super single bond (R Os–Os
= 4.60 Å) is longer than the super triple bond (R Os–Os
= 3.92 Å). Moreover, in their electronic shells, more electrons are localized within the super triple bonds between superatoms, resulting in higher electronic density, where can be a potential reactive site for electrophilic reagents.7,41

Finally, we extend the superatomic framework to one-
dimensional nanowires following the same bonding rule. Figure 8a shows the optimized geometry of the [PtAu6(AuCl3)]
nanowire. The unit cell of this gold nanowire contains two face-sharing Pt@Au12 icosahedrons, with the optimized lattice constants of a = b = 50 Å and c = 8.43 Å. The super bond length between two icosahedral SAs (4.22 Å) in this nanowire is almost the same as a super single bond (4.23 Å) in the [PtAu12(Au6Cl19)] (2) cluster.

Solid-state adaptive natural density partitioning (SSAdNDP)68 analysis is carried out to gain the bonding pattern in the
[PtAu6(AuCl3)]
nanowire. The bonding analysis is performed in three icosahedral SAs with a 2 × 1 × 1 supercell, and the results identify that there are two 13c−2e super LPs (super pπ and pσ) in each Pt@Au12 SA and one 2sc−2e super σ bonding orbital is formed by sp hybrid orbitals of adjacent SAs to achieve electronic shell closure, as shown in Figure 8b. As expected, this nanowire is a semiconductor with a band gap of 0.7 eV (PBE), because valence electron pairs are localized in either one superatom as super LPs or between two superatoms as super bonds. However, in the pure gold nanowire with similar face-sharing geometry, reported by Whetten et al.,36 there is one more valence electron in each icosahedron, in which the electronic shell closure of the SVB model cannot be satisfied; thus, this nanowire is metallic.

Ab initio molecular dynamics (AIMD) simulations are further performed to confirm the thermal stability of the
[PtAu6(AuCl3)]
nanowire. The unit cell (24 Au atoms, 2 Pt
atoms, and 12 Cl atoms) is adopted as the initial configuration. Energy fluctuation depending upon the simulated time at 300
K and the snapshot of Pt@Au12 after a 10 ps AIMD simulation

Figure 8. (a) Geometry of ligand-protected face-sharing [PtAu6(AuCl3)]
nanowires, (b) AdNDP localized bonds and ONs of three icosahedral
Pt@Au12 units in a 2 × 1 × 1 supercell (PBE/def2svp), and (c) electronic band structure of [PtAu6(AuCl3)]
(PBE) (Au, yellow; Pt, gray; and Cl, green).
are plotted in panels b and c of Figure 9. It can be observed that the structure of the nanowire maintains integrity with only a slight disturbance of individual atoms during the 10 ps AIMD simulation, indicating its good thermal stability at room temperature.

In conclusion, we extend the SVB model to the possibility of tri- and tetra-superatomic molecules formed by \((M@Au_{12})_n\) \((M = Au, Pt, Ir, and Os, and n = 3 and 4)\) icosahedral units. Chemical bonding analysis reveals that the bonding framework of tri-superatomic molecules \([M_3Au_{30}(Au_{18}Cl_{30})]\) \((M = Au, Pt, and Os)\) \((1-4)\) is similar to \(\text{Cl}^{-}, \text{OCl}_2, \text{O}_3, \text{and CO}_2\), and the tetra-superatomic molecules \([M_4Au_{39}(Au_{21}Cl_{36})]\) \((M = Au, Ir, and Os)\) \((5 and 6)\) are analogues of \(\text{N=C-C=N and Cl-C=C-Cl}\). The lengths of super triple bonds are shorter than those of super single bonds in these tetra-superatomic molecules, which is another evidence for their superatomic bonding character. Subsequently, the one-dimensional \([\text{PtAu}_9(AuCl_2)_3]_n\) superatomic nanowire is designed following the same bonding rule, in which each icosahedral \(\text{Pt@Au}_{12}\) SA forms one super \(\sigma\) bond with its adjacent one. The geometric and electronic stability of this nanowire has been confirmed, and the length of its super \(\sigma\) bond is approximate to a single super bond in the \([\text{PtAu}_9(AuCl_2)_3]\) \((2)\) cluster. This paper explores electronic rules for cluster assembling from superatoms to multi-superatomic molecules and superatomic nanowires, which gives references for their experimental synthesis.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.2c00007.

Computational details and relative references, comparison of Kohn–Sham molecular orbitals for \([Au_{13}(AuCl_{18})]^−\) and \(Cl^−\) (Figure S1), structures and localized bonds of the \(\text{Au}_{17}\) core in \([\text{Au}_{13}(\text{PPh}_3)_3(\text{SR})_3\text{X}_3]^+\) (Figure S2), and Cartesian coordinates of structures 1–6 reported in this work (PDF)

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Notes
The authors declare no competing financial interest.

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