

A Unified Framework for Understanding the Structure and Modifications of Atomically Precise Monolayer Protected Gold Clusters

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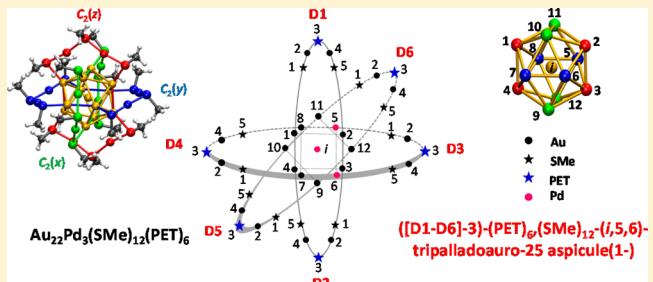
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S Supporting Information

ABSTRACT: Atomically precise monolayer protected clusters are molecules comprising a few-atom cluster core of a noble metal, typically Au or Ag, surrounded by a protective layer of ligands, exhibiting many special optical, electrical, catalytic, and magnetic properties, and are emerging as important materials in biology, medicine, catalysis, energy conversion and storage, and sensing. The structural diversity of these clusters or aspicules, as we definitively term them, meaning shielded molecules, combining the Greek word *aspis* (shield) with molecule, is rapidly increasing due to new compositions and modification routes such as ligand-exchange, alloying, or supramolecular functionalization. We present a structural analysis of the most stable cluster of this kind, $\text{Au}_{25}(\text{SR})_{18}$, and propose a Borromean rings diagram for the cluster, showing its topological configuration of three interlocked (Au_8S_6)-rings. This simplified two-dimensional diagram is used to represent its structure and modifications via ligand or metal atom substitution uniquely. We enumerate and name its isomers with two-ligand or metal atom substituents. Among the several structural insights obtained, the identification of the Borromean rings-interlocked configuration in $\text{Au}_{25}(\text{SR})_{18}$ may explain its high geometric stability and indicate a possible general unified structural viewpoint for these clusters without the division between core and staple motifs. On the basis of our structural analysis, we developed a structure-based nomenclature system that can be applied to both describe and understand the structure and modifications of gold thiolate clusters, $\text{Au}_M(\text{SR})_N$, and is adaptable to the general case of $\text{M}_M(\text{X})_N$ (M , metal and X , ligand). The application of structural analysis and diagrams to $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$, revealing the possible formation of the cluster core by stacking or growth of rings of metal atoms, is also presented.



1. INTRODUCTION

Over the past two decades, since the pioneering work of Brust and Shiffrin on the synthesis of small alkanethiolate monolayer protected clusters of gold,¹ noble metal clusters of ultrasmall size consisting of a few (~ 10 to ~ 1000) atoms surrounded by a monolayer of organic ligands have evolved into an area of intense research.^{2–11} A significant advancement in this area came in late 1998 after the isolation of the very first molecularly precise clusters of this kind, $\text{Au}_{28}\text{SG}_{16}$, by Whetten and co-workers¹² (where SG is glutathione, later reassigned as $\text{Au}_{25}\text{SG}_{18}$ by Tsukuda and co-workers¹³), composed of an Au(0) core and protected with ligands; the cluster itself was synthesized from Au(I)SG polymers. In the subsequent years, research on this class of materials gained momentum.^{6,11,14–18} Properties such as unique absorption,^{6,12,19,20} luminescence,^{10,21–25} unusually strong chiroptical activity,^{26–29} electrical^{30–32} and catalytic properties,^{33–35} magnetic properties,^{36–39} etc., proved these clusters to be unprecedented and useful for a host of potential applications.^{5,7,9–11,40} In that perspective, various synthetic approaches have been developed

to make clusters with different core sizes, surface functionalities, and chemical compositions.^{5,41–47} The molecular science of these materials became even more important as their structures became known from single crystal studies, for example, through the efforts of Kornberg,⁴⁸ Murray,⁴⁹ Jin,^{50–54} Dass,^{55–60} Tsukuda,⁶¹ Bigioni,⁶² Zheng,^{63–66} Ackerson,^{67,68} Zhu,^{69–71} Wang,^{72,73} Maran,⁷¹ Simon,⁷⁴ Wang,⁷⁵ Bakr,⁷⁶ Liu,⁷⁷ and co-workers. Because each composition has a unique structure that depends on the number of metal atoms and ligands, a large variety of fascinating structures exist, but understanding their origin and predicting them remain important challenges that are still not resolved completely.

Modifications may involve changes in the metal core as in the case of $\text{Au}_{25-x}\text{M}_x(\text{SR})_{18}$, where M is a metal atom, or in the ligand as in the case of $\text{Au}_{25}(\text{SR}_1)_{18-x}(\text{SR}_2)_x$,^{80,81} where SR₁ and SR₂ are two different thiols. Mixed ligand-exchanged

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clusters containing a distribution of chemical compositions of $\text{Au}_{24}\text{Pd}(\text{SR}_1)_{18-x}(\text{SR}_2)_x$ have been separated and isolated using high-performance liquid chromatography (HPLC), and evidence of isomers in ligand-exchanged clusters was acquired.⁸⁰ Different regioisomers of $\text{Au}_{38}(\text{SR}_1)_{23}(\text{SR}_2)_1$ have also been identified and isolated using HPLC.⁸² Similarly, a small number of experimental studies have determined the precise positions of the substituted ligands or metal atoms by X-ray diffraction or other techniques,^{55,57,67,68} and structural studies by Ackerson and co-workers have found the precise position of ligands exchanged for $\text{Au}_{25}(\text{SR}_1)_{16}(\text{SR}_2)_2$ and also for $\text{Au}_{102}(\text{SR}_1)_{40}(\text{SR}_2)_4$.⁶⁸ A combined experimental and theoretical approach to gain more information on the exact substituent locations may also be fruitful, for example, in the cases of *R*-1,1'-binaphthyl-2,2'-dithiol (BINAS) ligand-exchanged $\text{Au}_{38}(\text{SR})_{24}$ ⁸³ and copper doping of $\text{Au}_{25}(\text{SR})_{18}$.^{79,84} With the growth of this new family of molecules with associated chemistry, one requires a system to describe the structure and composition, and also to precisely describe the positions of atoms and their connectivity both in the core as well as in the outer shells of these clusters.

Being distinct from both small gas-phase atomic clusters and their monolayer protected nanoparticle counterparts,^{85,86} these clusters may be rightly regarded as molecules because they consist of a finite aggregate of atoms which are chemically bonded to each other, have well-defined and measurable physical and chemical properties, and also form the building blocks of molecular crystals. Hence, the term nanomolecule is frequently used for them. A variety of other names have been used to describe this class of molecules as a whole such as monolayer protected clusters, ligand-stabilized clusters, clusters, nanoclusters, quantum clusters, superatoms, faradaurates, fluorescent nanoparticles, molecular clusters, atomic clusters, etc., to list a few. However, no consensus has been reached on what to call these molecules, and new names are constantly being generated. Many of the names have deficiencies mostly due to either being nonspecific to this class of molecule, and thus are nonunique; for example, the term monolayer protected clusters (MPCs) is also used to describe larger nanoparticles. The ubiquitous term “cluster” has its principal application to atomic/molecular assemblies, typically in the gas phase, and considering the molecular nature of these systems we find that this name is unsuitable for them. The addition of prefixes to yield names such as metallic clusters, molecular clusters, etc., also fails to remedy the situation. IUPAC nomenclature names often include a compact single-word name for the category of molecules such as in fullerene nomenclature.⁸⁷ A unique and specific name is therefore desirable to describe this class of materials that captures their two defining characteristics, first that they are molecules, and second that they have a protecting layer of ligand groups peripheral to an inorganic core. The ligand layer is crucial to the stability of the entire molecule, as it prevents the metal cores from etching or aggregating to form small metal complexes and larger metal nanoparticles, respectively, during synthesis in solution (generally) as well as in the solid phase, and protects the core from reactive molecules and ions. Furthermore, electron transfer from the core to the ligands and reverse is crucial to both the electronic and the geometric stability of the monolayer protected clusters, which leads to the appearance of “magic numbers” of core atoms. Electronic interaction of the core and the ligand layer is thus essential for the stability of the system as a whole. All of these reasons lead us to propose a name capturing the

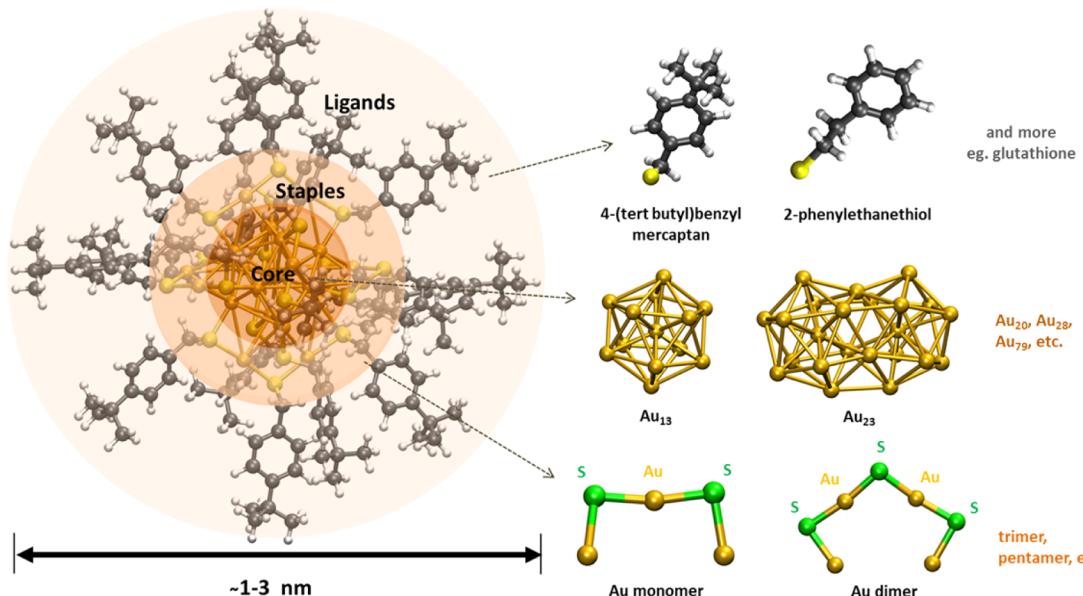
molecular character of an entity, which itself is protected with molecules. We propose the compound term “aspicule” for this class of molecules; the name is derived by combining the Greek root word *aspis* meaning shield and the word molecule, to denote a shielded molecule. The name aspicule may be extended to other protected metal clusters, composed primarily of other metals rather than gold and silver, and for which the shielding effect of the ligands is crucial to their stability, for example, those containing Pd,⁸⁸ Al, and Ga.^{88,89} We note that the term metal aspicule may be a yet more precise description, and its derivatives such as gold, silver, and palladium aspicles, and so on. We appreciate that several other names already in use such as (nano)clusters, quantum clusters, nanomolecules, faradaurates, etc., may continue to be used. Hereafter, we refer to monolayer protected clusters as aspicles in this Article. We may define the term aspicule precisely to mean those entities that have a molecular formula and consist of a closed cage metal cluster of more than a few atoms in their central region bonded to a surface arrangement of ligands or atoms or ions, which shield the inner metallic core structure from destructive chemical interactions in the solution and solid states. This definition distinguishes aspicles from their larger monolayer protected nanoparticles and nanocrystal counterparts composed of thousands of atoms, which do not have precise molecular formulas (at the current experimental capability, especially using mass spectrometry), but have an overall morphology and lattice arrangement with associated dimensions, and it also distinguishes them from smaller noble metal complexes.

We investigated the structure, symmetry, and network topology of the three aspicles, $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, and $\text{Au}_{102}(\text{SR})_{44}$. We found simplified structural representations, derived structural insights from them, and produced labeled diagrams of these molecules to represent their modifications. As a secondary aspect, we also created an overall framework in the form of a structure-based nomenclature, which integrates our structural analysis and provides names for the structures and their modifications in the general case of $\text{Au}_M(\text{SR})_N$ or $\text{Au}_M(\text{X})_N$. We emphasize that the structural analysis and its insights are the central aspect of this Article, and the nomenclature is only a byproduct.

We begin with a description of the general structure of gold thiolate aspicles, and develop simplified representations of the structure of $\text{Au}_{25}(\text{SR})_{18}$ in section 2.1. This is followed by a systematic presentation of the nomenclature and precise terminologies in sections 2.2–2.5, which can be applied to describe the structure of any gold thiolate aspicule or its chemical modifications at different levels of structural detail. Modifications of $\text{Au}_{25}(\text{SR})_{18}$ are represented using locants and structural diagrams for cases of ligand and metal atom exchange, their two-substituent isomers, and specific supramolecular/conjugated interactions (section 2.6–2.8). Sections 2.9 and 2.10 show how we applied this structural analysis to $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$. Last, in section 2.11, we review some of the main structural insights gained and their implications to the general structure of aspicles.

2. METHODOLOGY, RESULTS, AND DISCUSSION

2.1. Aspicule Structure and Simplified Structural Representation of $\text{Au}_{25}(\text{SR})_{18}$. The structure of an aspicule may be represented as three concentric shells of atoms: the protective shell of ligand R-groups, an intermediate mantle, and the inner metal core (Scheme 1).

Scheme 1. Generic Structure of Gold Thiolate Aspicules^a

^aSchematic of the shell structure of an aspicule (left), with the size of a typical $\text{Au}_{25}(\text{SR})_{18}$ aspicule (1–3 nm) marked. Examples of the constituent structures of the core, staple, and ligand R-group regions with their terminating sulfur atoms are shown (right).

For example, in $\text{Au}_{25}(\text{SR})_{18}$, the core consists of an Au_{12} icosahedron, plus a single gold atom at the center, while for Au_{38} it is a face-sharing bi-icosahedron with two gold atoms at the center of each icosahedron. The second shell or mantle is the structure that is found between the core and the ligands, which follows the “divide and protect” scheme,⁹⁰ in which the staple-like structures containing both metal and chalcogen (usually sulfur) atoms project out from core atoms and then bond back to a different core atom. This coordinating atom forms bonds linking the core atoms and staple metal atoms, which is sulfur in the case of thiolate ligands. Different sizes of staples (oligomeric forms), which have the general formula $-(\text{S}-\text{Au})_n-\text{S}-$ consisting of repetitive units of the monomer ($\text{S}-\text{Au}$) and a single terminating sulfur atom at one end, are named according to the number of repeating $-(\text{S}-\text{Au})-$ units contained in the staple: monomer $-\text{S}-\text{Au}-\text{S}-$,^{48,51} dimer $-(\text{S}-\text{Au})_2-\text{S}-$,^{49,50} trimer $-(\text{S}-\text{Au})_3-\text{S}-$,⁹¹ tetramer $-(\text{S}-\text{Au})_4-\text{S}-$,⁹² pentamer $-(\text{S}-\text{Au})_5-\text{S}-$,⁹¹ and heptamer $-(\text{S}-\text{Au})_7-\text{S}-$,⁹¹ with smaller staple sizes being found typically in the larger core sizes of aspicules. There are also instances of single sulfur atoms ($-\text{S}-$) bridging two core atoms.^{59,93,94} The third and outermost layer is the ligand shell where the R-groups of organic thiolates ($\text{RS}-$) of phenylethanethiol (PET), glutathione (SG), 4-*tert*-butylbenzyl mercaptan (BBSH), etc., are bonded to the sulfur atoms in the staples or directly to sulfur atoms that bridge the core atoms. At the outset, we make some general simplifications about the structure. First, we need only consider (in most cases) the structures of the core and mantle shells omitting the ligand R-groups because chalcogen (S, Se, Te) atoms represent the termini of the ligands.

This reduces the total number of atoms to 43 and 62 for $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Au}_{38}(\text{SR})_{24}$, respectively, for example. Second, aspicule structures from experiments are not perfectly symmetric; they exhibit variations in bond length, angles, and also a dihedral distortion in the staples, for example, in $\text{Au}_{25}(\text{SR})_{18}$.⁵⁰ Here, we ignore these minor distortions in the geometry and assume symmetric core and staple structures.

Third, we neglect orientation of the ligand with respect to the staples (*cis-trans*), and also its internal conformation. The directions of the S–C bonds, relative to the staples, may be included at a later stage to give a description of their *cis-trans* isomerism and the inversion symmetry of the coordinating atom–carbon atom (S–C for thiolates) bond directions on opposite sides of a pair of coplanar staples, as found for example in $\text{Au}_{25}(\text{SR})_{18}$. Similarly, the torsional angles of the first ligand C–C bond with respect to the staple Au–S bonds and its own internal torsional angles may be specified using terms such as trans and gauche(\pm). We consider only gold thiolate (Au–S) aspicules in our examples, but our methods could be applied with some additional modifications to take account of different types of staple motifs for the case of other metals such as silver and different coordinating atoms by substitution of S for Se, P, or Cl, where in the latter two cases there are no staple motifs, for example, in the name.

For concreteness, we will write as though the ligand is methylthiol(ato) (SMe) and the substituted ligands are always PET (2-phenylethanethiol(ato)), and similarly we designate the metal substituent by Pd (palladium) in our examples. Although multiple Pd substituents are a rarer case than Ag substituents, for example, we have used Pd to avoid confusion between majority silver and gold aspicules, which generally have marked structural differences. We assume for simplicity that the charge of the modified aspicules that we present as examples is the same as that of the parent aspicule.

The first objective of our structural analysis is to find a simplified representation of the structure in the form of a diagram, with unique positional labels (locants) for (a) the core atoms, (b) the staples, (c) the ligands, and (d) the staple metal atoms. For this purpose, we made extensive use of the molecular building and visualization software Avogadro⁹⁵ and VMD⁹⁶ for structural manipulation and visualization. The core and staple structure is obtained from the crystal structure/DFT-optimized crystal structure by extracting the entire molecule from the crystalline unit cell, and subsequently

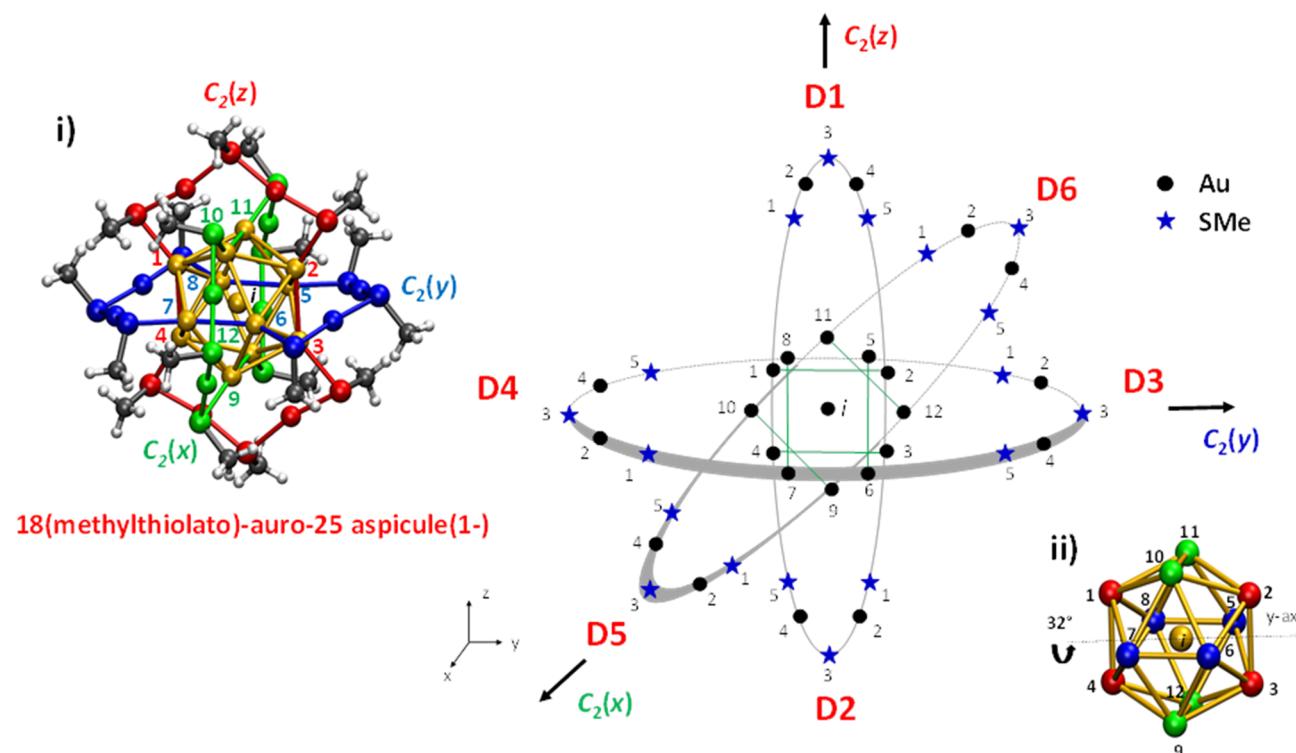


Figure 1. Borromean-rings diagram of $\text{Au}_{25}(\text{SMe})_{18}$. The rings formed by pairs of coplanar staples are shown as ellipses. Gold atoms are shown by black dots, and dark blue stars represent the SME ligands whose positions are taken to be identical with their sulfur atom. The core Au atoms are numbered from 1 to 12, and the staple atoms are numbered clockwise from the end of the staple, from 1 to 5. The lines that join core Au atoms on opposite ends of the same staple are shown by the green lines. The three perpendicular C2 axes are marked with the associated Cartesian axis direction in parentheses. The staple directions are labeled by the six staple locants D1 to D6, marked in red. Inset (i) shows a 3D visualization of the ring structure of the core and staples of $\text{Au}_{25}(\text{SR})_{18}$ aspicule, with each (Au_8S_6) -ring consisting of two coplanar staples and the core atoms that are bonded to these staples. The three rings are colored red, blue, and green, and the numbers of the core atoms are marked; the aspicule name for $\text{Au}_{25}(\text{SR})_{18}$ is shown in red below it. The core Au atoms and also Au–Au bonds that are not part of the rings are shown in gold, while the other atoms are colored according to which ring they are part of. Inset (ii) shows a close-up of the numbering scheme of the core atoms marked on the edge-projection of the core icosahedron. The arrow indicates the angle of the anticlockwise rotation about the y -axis, needed to bring the icosahedron into a face-projected view of the face defined by the atoms 6, 7, and 9.

isolating the gold and sulfur atoms from the model by replacing the R-group in the crystal structure by Me or removing it completely, and we refer to the latter as the core and mantle (staple) structure. Initially, a detailed consideration of symmetries and the orientation of $\text{Au}_{25}(\text{SR})_{18}$ was carried out, which is shown in **Supporting Information (SI) 1**.

The general approach we follow is to first simplify the structure and bonding network by focusing on different groups of atoms and bonds, and also selecting representations that capture the entire structure as simply as possible. We considered various possible structural representations and labeling schemes for Au_{25} , such as polyhedral shells (Figure S2 in SI 2), core and staple motif $\text{Au}_{25}(\text{SR})_{18}$ with Cartesian locant labels for atoms (Figure S3 in SI 2), and the molecular graph (Figure S4 in SI 2). The simplest representation we found was based on a simplification of the core and staple structure, which, apart from the central gold atom, shows the staples and only the core Au–Au bonds that lie on three (Au_8S_6) -rings, leading to the diagram shown in Figure 1, and this figure is the central idea of this Article. This simple topological representation is based on a projection of the three-ring structure of $\text{Au}_{25}(\text{SR})_{18}$, and shows all of the essential atoms and the octahedral symmetry; Figure 1 represents the central result of this Article. Figure 1, inset i, shows a 3D visualization of the core and staple structure of $\text{Au}_{25}(\text{SR})_{18}$.

where there are three perpendicular (Au_8S_6)-rings, colored red, blue, and green, with each ring consisting of two coplanar staples and the four core atoms to which their ends are bonded. The presence of these (Au_8S_6)-rings has been noted earlier from the crystal structure;⁴⁹ however, we examined their relative arrangement more closely. We found that the arrangement of these rings is identical to the configuration of interlocked rings known as the Borromean rings. The Borromean rings satisfy the condition that the removal of one ring causes the other two to fall apart, and no two rings are linked together and are therefore the smallest possible “Brunnian link” having only three components (rings). The rings can be viewed as a cover over the central gold atom. The physical significance of these rings is discussed in detail in section 2.11. This ring representation is obtained by omitting the core Au–Au bonds that are not part of the red, blue, and green rings as shown in inset (i). The Borromean-rings condition can be verified by direct observation of inset i of Figure 1. If we imagine the core Au–Au bonds that are not part of the rings (shown in gold) and the central gold atom are not present, then the removal of the green ring allows us to lift the red ring upward and outside of the plane of the blue ring, thus freeing these two rings, which would otherwise be impossible. Structural manifestation of additional stability due to ring

structure is discussed in section 2.11, which renders additional proof to its existence and significance.

Projecting the three-dimensional ring structure onto the plane and representing each ring as an ellipse, and adding symbols for atoms in the appropriate places results in the Borromean-rings diagram at the center of Figure 1. We label each ring of the structure by the symbol of the symmetry axis passing through the bridging sulfurs that lie on the ring, that is, $C_2(y)$ for the blue ring, $C_2(z)$ for the red ring, and $C_2(x)$ for the green ring. The central parts of the ellipses represent the core, and the ends of the ellipses represent the staples. The gold and sulfur atoms are represented by “●” and “★”, respectively, placed according to their connectivity, and we note that the bond distances are not to scale in this schematic representation.

The three-dimensional effect in Figure 1 is brought out by using thicker lines for those ellipse-edges that are projecting out of the plane of the paper, while those that are going into the plane of the paper are shown by thin dashed lines, in the same way as in stereochemical diagrams of molecules. A close-up view of the icosahedral core in its edge projection with core atoms numbered is shown in inset (ii) of Figure 1. We found that this Borromean-rings diagram has the advantage that it allows one to easily visualize ligand-exchanged and alloyed $\text{Au}_{25}(\text{SR})_{18}$ aspicules. Step-by-step instructions for drawing the diagram by hand are provided in Scheme S1 in SI 4. It is possible for a Borromean-rings type of diagram to be extended to $\text{Au}_{144}(\text{SR})_{60}$, because the core and staple structure would most likely be identical to that of the experimentally determined, $\text{Au}_{144}\text{Cl}_{60}$ structure, which contains six ($\text{Au}_{20}\text{Cl}_{10}$)-rings surrounding a central 24-gold-atom vertex-capped icosahedron.⁹⁷

For the purpose of describing modifications precisely, we must assign to each metal atom or ligand of Figure 1 (or, equivalently, a sulfur atom) a unique label, and this assignment is described below. The term substituents is used to denote modifications of the ligands, metal atoms on a staple, or metal atoms in the core, and their positions are all specified using the positional labels of substituents, or locants. The parent structure of $\text{Au}_{25}(\text{SR})_{18}$ has locants as follows: The locants for each of the staples consist of the letter D for dimer, indicating the number of gold atoms in the staple, followed by the staple number that uniquely identifies it. The three C_2 axes have been rotated to coincide with the Cartesian axes as shown in Figure 1. For $\text{Au}_{25}(\text{SR})_{18}$ shown in Figure 1, the staples are labeled as D1 and D2 for the staples pointing in the z- and z'-directions (where the prime denotes the negative Cartesian direction), D3 and D4 for the staples pointing in the y- and y'-directions, and D5 and D6 for the staples in the x- and x'-directions. The core atoms are labeled according to which staple they are bonded to, so that core atoms 1, 2 are associated with staple D1, atoms 2 and 3 with staple D2, atoms 4 and 5 with staple D3, and D4, etc. Each atom on a staple is given a positional number (“staple atom number”), in sequence (as in the IUPAC nomenclature of inorganic chains), beginning with 1 for the sulfur atom at the end of the staple bonded to the core atom that has lowest locant, and counting clockwise the atoms in sequence around the dimer staple. The locants of the ligands are formed by the staple locant followed by a hyphen and the staple atom number of the sulfur atoms (1, 3, or 5). Hence, the sulfur atoms on the D1 staple, for example, are referred to as D1-1, D1-3, and D1-5, while the staple metal atoms are referred to as D1-2 and D1-4.

We used the Borromean-rings diagram to represent the ligand-exchange and alloy modifications, and their respective isomers, of $\text{Au}_{25}(\text{SR})_{18}$ (see sections 2.6 and 2.7). On the basis of this labeled diagram, we created a structure-based nomenclature as a tool for understanding the structure, to refer to the positions of the substituent atoms, and also to name the structure and their modifications precisely in the general cases of $\text{Au}_M(\text{SR})_N$ and $\text{Au}_M(\text{X})_N$.

2.2. Development of a Structure-Based Nomenclature. Precise and systematic structure-based names for these molecules would also enable the structure and details of ligand-exchanged and alloyed molecules to be conveyed accurately and efficiently in a standardized format. There is also a need to depict them on paper, retaining the essential structural details. These requirements are fulfilled by a structural nomenclature, which provides a framework within which it is possible to associate with a molecule a unique name containing essential structural aspects such as the bonding topology and geometry, and compositional information.

Structure-based nomenclatures also serve as a framework and a tool for understanding the molecule itself and its modifications, because the structural representations shown in the diagrams also carry physical significance. By means of the unique labels (locants) for the atoms, we may specify the positions of modifications in the name, even in cases where modifications break the symmetry. The lack of structural nomenclature is not exclusive to monolayer protected clusters but applies to nanomaterials as a whole, and some effort has been initiated to create a unified framework and classification of nanomaterials.⁹⁸ IUPAC (International Union of Pure and Applied Chemistry) nomenclature exists for certain nanomaterials such as fullerenes⁸⁷ and boranes,⁹⁹ and we therefore anticipate that nomenclature would be useful in the case of this category of materials as well.

The following criteria were forefront while developing this nomenclature: It should (i) be symmetry based, (ii) be universal and be able to describe the structure and/or modifications of any aspicule, (iii) have resemblance to IUPAC nomenclature, and (iv) be simple enough to use and remember, so that it would be useful to workers in the field. The latter condition also entails that the resulting names of aspicules should be as succinct as possible, and that diagrams of their structure should be drawable by hand, if possible, after some training. Throughout, we follow the general IUPAC convention of placing the substituent locants as a prefix to the name of the substituent with a hyphen between the prefix and the substituent name. Three stages are involved in the development and application of a structure-based nomenclature.

(1) Structural and symmetry analysis: Finding a suitable structural representation for the aspicule so that a diagram of the structure can be drawn. Selecting a standard symmetry-based orientation. This is an important aspect as a unique representation is needed to locate atoms.

(2) Locant assignment: Assigning unique labels to the relevant parts of the structural diagram in a systematic way so that modifications can be named.

(3) Naming: Assigning names that contain information (descriptors) about different structural, compositional, and molecular properties, for both the parent structure and its modifications. Creation of syntax for linking these descriptors to form the names.

On the basis of the three-shell description, a name that completely describes the parent structure of an aspicule would contain the following information.

(1) Core: The geometric shape of the core and its composition.

(2) Staples: The number and size of each type of staple and the connectivity of the atoms of the staple to the core atoms at their ends.

(3) Ligands: The number and type of each ligand R-group and their positions of attachment on the staples. Stereodescriptor prefixes may be used for *cis-trans* isomerism of the ligands with respect to the staple, and their internal conformation.

(4) Other details: The total number of metal atoms, the name of this class of molecules (aspicule), and the electrical charge; the latter two may be appended to the name as part of a final suffix. The geometric shape of the core and the principal symmetry axis, and the formula name of the crystal counterion, may also be added in parentheses as an additional suffix.

Stereodescriptor prefixes for the intrinsic chirality of the core and staple structure may be added to the front of the name, describing the type of isomerism, which may be configurational, the latter being defined by the relative position of the substituents on the staples.

We have developed a complete structural nomenclature, which we call “aspicule structural nomenclature”. It incorporates all of the above aspects of the structure, and is presented in SI 5. Describing the connectivity of the staples to the core atoms increases the lengths of the structural names, and detailed names with this information intact may be found in SI 5 and Tables S7 and S10 in SI 9. For this reason, we have chosen in this Article to describe the modifications of parent aspicules, and we have condensed the names by omitting the unnecessary details of the structure. We term this reduced version “aspicule nomenclature”, and the resulting names are “aspicule names”. In aspicule nomenclature, a parent aspicule name has three parts: the first part describes the ligands consisting of their type and number, while the second part describes the names of the metal present, both in the core and in the staples, and includes the total number of metal atoms. The third part of the name specifies the name of the family of molecules (aspicule) and the electrical charge. Structural details such as geometric isomerism and chirality can be included as prefixes to the front of the whole name.

The nomenclature has been developed to be valid for any gold thiolate aspicule and utilizes the core and staple motif picture of the structure. Before describing the nomenclature in detail, we present as an introduction the name for $\text{Au}_{25}(\text{SMe})_{18}$ according to our nomenclature, which is 18(methylthiolato)-auro-25 aspicule(1-) or $(\text{SMe})_{18}\text{-auro-25}$ aspicule(1-), in its condensed form. The name for $\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$, based on the locants of Figure 1, which has two PET ligands exchanged at the bridging positions on the D1 and D2 staples, is (D1-3,D2-3)-di(2-phenylethanethiolato),16(methylthiolato)-auro-25 aspicule(1-) or, in its condensed form, (D1-3,D2-3)-(PET)₂(SMe)₁₆-auro-25 aspicule(1-). In this name, the locant prefix (D2-3,D2-3) denotes that the ligand exchange occurs at the two bridging sulfur atoms on opposite dimer staples in the z - and z' -directions, D1 and D2. We now systematically present the aspicule nomenclature in sections 2.3–2.5, apply it to modifications and isomers of $\text{Au}_{25}(\text{SR})_{18}$ in sections 2.6–2.8, and finally in sections 2.9 and 2.10 we show how it can be applied to $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$ and their modifications.

2.3. Symmetry Axes, Orientation, and Diagrams.

Locants are generally assigned with respect to a single symmetry axis by counting atoms lying in the parallel planes lying perpendicular to the symmetry axis.

2.3.1. Principal Symmetry Axis.

Before locant assignment can be carried out, the aspicule symmetry axes, around which the numbering of staples and core atoms will take place, must be identified and must be oriented in a standard way. Usually, the highest axis of rotational symmetry may be chosen as the principal axis about which numbering of the staples and core atoms is carried out. The chosen axis of rotational symmetry should, if possible, apply to both the core and the staples of the aspicule, because these two parts of the structure may not share all of the axes of rotational symmetry present. If any of staples do not share the core symmetry axis, but are nevertheless spatially distributed around this axis, we may choose the highest rotational symmetry axis of the core as the principal one. The principal symmetry axis is oriented to coincide with the z -axis, with its top end being associated with the z -direction.

2.3.2. Orientation and Diagram.

The aspicule should then be rotated into a unique standard orientation, which is as unique as its symmetry permits. This could be achieved by bringing other symmetry axes or some other distinctive structural feature, such as a particular staple, into a fixed orientation with respect to the Cartesian axes.

Visualization of the 3D structure of a molecule may serve as a diagram, after reduction of the structure to simpler elements such as rings as we demonstrated for $\text{Au}_{25}(\text{SR})_{18}$ so that a two-dimensional diagram can be drawn by hand. In the special case where there are three perpendicular C_2 axes as in $\text{Au}_{25}(\text{SR})_{18}$, it is preferable to align these with respect to standard Cartesian axes, to show the octahedral staple symmetry clearly, and this view may sometimes be preferred over the tomographic representation about a single principal C_3 axis (Figures S5 and S6 in SI 3). For the C_2 axes scheme, we identify three perpendicular planes, which contain the $C_2(x)$, $C_2(y)$, and $C_2(z)$ rings of atoms, and the numbering of staples and core atoms can proceed around the rings that lie perpendicular to each of these three axes.

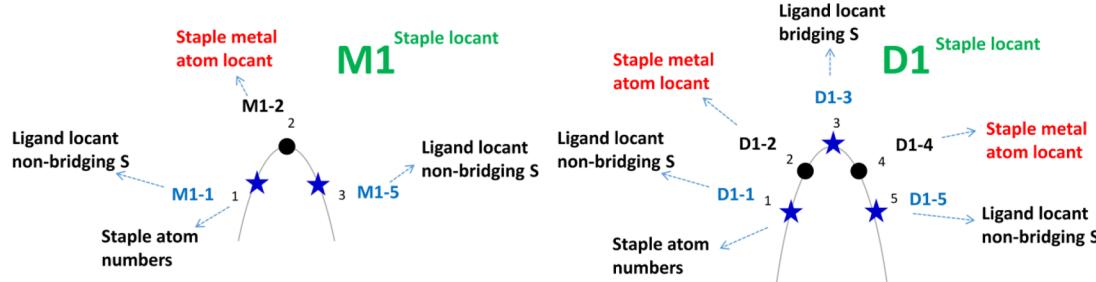
2.4. Aspicule Locants and Their Assignment.

The locants for the staples, ligands and staple metal atoms, and core atoms and their assignment schemes are described in sections 2.4.1–2.4.3.

2.4.1. Staple Locants.

The locants of the staples have two parts, first, one or two letters that correspond to the type of staple determined by the number of gold atoms it contains, and this is followed by the identification number of the particular staple. The following upper case letters are used: M for a monomer staple, D for a dimer staple, and TR for a trimer staple. Others are TE (tetramer), P (pentamer), HX (hexamer), HP (heptamer), O (octamer), N (nonamer), D (decamer), U (undecamer), DO (dodecamer), etc.; the two-letter symbolism is used in some cases to avoid confusion. A slightly more precise way of notating the staple types would be MS, DS, TrS, etc., where S stands for terminating sulfur; however, for simplicity we prefer to omit the S.

Two further cases arise when the ligands are bonded to the core rather than the staples; first, when the ligand (SR) bridges two core atoms, we use the Greek letter μ , as it is conventionally used to denote bridging atoms in IUPAC inorganic nomenclature, in the same manner as the staple type letter, so a set of three bridging ligands would be labeled $\mu 1$, $\mu 2$, $\mu 3$, etc. Second, if the ligand is only bonded to a single core

Scheme 2. Assignments of Ligand and Staple Metal Atom Locants in Monomer and Dimer Staples^a

^aTaken to be staples M1 and D1 in this example.

atom, we use the letter C, which stands for core, instead. The assignment of the identification numbers of these ligands follows the same procedure as that for the staples. Staples of the same type are numbered in separate sequences, for example, D1–D6 for the six dimer staples of $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Au}_{38}(\text{SR})_{24}$, and M1–M3 for the three monomer staples of $\text{Au}_{38}(\text{SR})_{24}$. Depending on the types of symmetries present, scheme 2.4.1.1 or 2.4.1.2 can be adopted to assign the staple locants.

2.4.1.1. Single Principal Symmetry Axis. 2.4.1.1.1. Staple Groups. We may consider staples as being grouped, first, by the fact that their bridging sulfur atoms are located on the same planes perpendicular to the principal axis or, second, by the different rings of core atoms to which their ends are bonded.

2.4.1.1.2. Sense of Staple "Rotation". The direction of "rotation" of a staple can be defined from the projection of the aspicule structure onto a plane perpendicular to the symmetry axis as to whether a clockwise or anticlockwise rotation is needed to bring the core atom bonded to the sulfur atom of the staple with the lowest staple atom number into coincidence with the core atom bonded to the sulfur atom with higher staple atom number on that staple.

2.4.1.1.3. Assignment of Staple Locants. The direction of assigning of the staples in a group is carried out according to the direction of rotation of the staples, being either clockwise (C) or anticlockwise (A). Numbering of staples in each group is carried out starting from the staple group at the top, and if the staples are rotating in clockwise fashion just to the right of the 12 o'clock position (in the x' -direction), counting clockwise around the principal symmetry axis. While for staples that rotate anticlockwise, these are numbered in an anticlockwise direction from the same 12 o'clock position. For example, in a case where there are six dimer staples located at the top and bottom regions of the C_3 axis, as in C- $\text{Au}_{38}(\text{SR})_{24}$, the staples would be numbered D1, D2, and D3 in the upper bridging sulfur plane and D4, D5, and D6 in the lower bridging sulfur plane. Hence, in special cases like this where all of the staples "rotate" in the same direction, this scheme is equivalent to numbering the staples winding both around and moving downward with respect to the principal symmetry axis.

2.4.1.2. Special Scheme: Three Perpendicular C_2 Axes for $\text{Au}_{25}(\text{SR})_{18}$. In $\text{Au}_{25}(\text{SR})_{18}$ due to the octahedral arrangement of staples, it is convenient to make further use of symmetry by using the three perpendicular C_2 axes, which, when this aspicule is rotated appropriately, correspond to the x , y , and z Cartesian axes that are oriented as in Figure 1. The staples that lie at either end of each Cartesian (C_2) axis are numbered in sequence according to the reverse order of the six Cartesian directions (so that the z -direction takes priority): z , z' , y , y' , x ,

x' . For $\text{Au}_{25}(\text{SR})_{18}$, the staples directions, respectively, staples D1, D2 are assigned to the z and z' ends of the $C_2(z)$ axis, D3 and D4 are assigned to the y and y' ends of the $C_2(y)$ axis, and staples D5 and D6 to the x and x' ends of the $C_2(x)$ axis.

2.4.2. Ligand Locants and Staple Metal Atom Locants. The ligand and staple metal atom locants are described in sections 2.4.2.2 and 2.4.2.3, and are formed by combining the staple locant with the appropriate staple atom number, described in section 2.4.2.1.

2.4.2.1. Staple Atom Number. Atoms on a staple are assigned a staple atom number, which counts the position of the atoms clockwise from the end of the staple that is bonded to the core atom with the lowest locant. The staple atom numbers for a monomer staple are 1(S_c), 2(Au), 3(S_c) (a total of three atoms), and for a dimer staple they are 1(S_c), 2(Au), 3(S_μ), 4(Au), 5(S_c) (a total of five atoms), where we have indicated the type of atom in brackets and use the subscripts " μ " and " c " to indicate bridging and nonbridging sulfur positions.

2.4.2.2. Ligand Locants. The position of a ligand on a particular staple is specified by appending to the staple label (D1, M1, etc.) a hyphen and the staple atom number of the sulfur atom, which is bonded to the ligand R-group. In the case where we have no staples, where the ligand or a terminating atom is directly attached to a core atom, we use the core locant as the ligand locant.

2.4.2.3. Staple Metal Atom Locants. The position of a staple metal atom is specified by appending to the staple locant a hyphen followed by the staple atom number of the metal atom substituent.

Scheme 2 illustrates the assignment of ligand and staple metal atom locants of the M1 and D1 staples, for example. The ligand locant D1-3 indicates the third atom counting clockwise around the staple, which is a sulfur atom in the bridging position on dimer staple 1, while D1-1 corresponds to the first nonbridging sulfur atom counting clockwise from the left end of the staple and D1-5 to the fifth atom counting clockwise from the left of the staple, which is the second nonbridging sulfur. Similarly, D1-2 and D1-4 indicate the positions of the two metal atoms on a dimer staple. Examples of monomer ligand and staple metal atom locants are M1-1, M1-2, and M1-3, which correspond to the ligand R-group bonded to the first nonbridging sulfur atom, the central metal atom, and the ligand R-group bonded to the second nonbridging sulfur atom on the staple.

2.4.3. Core Atom Locants. If the core of an aspicule consists of at least two concentric polyhedra, we term the innermost of these the central polyhedron, which we label separately. The locants of core atoms in the first noncentral polyhedron are

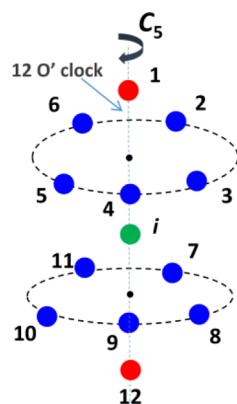
numbers, and if there is more than one such polyhedron comprising the core, we number the inner polyhedron first, and then for the next surrounding polyhedron, we begin the numbering again from one, and so on for each successive outer polyhedron. Furthermore, the locants of the atoms of the outer polyhedra are distinguished from each other by prefixing the number by a letter, which indicates the type of polyhedron or polyhedral fragments.

There are two possible schemes described in sections 2.4.3.1 and 2.4.3.2 of assigning core locants. The first is based on numbering around the principal symmetry axis, and is generally applicable, while the second is more convenient for small to medium sized aspicules with, for example, less than 44 metal atoms.

2.4.3.1. Core Ring Locants (Tomographic Representation). In this section, we describe a general procedure to carry out a tomographic sectioning of the structure around the principal symmetry axis and assign locants to the core atoms.

The numbering of the core ring locant procedure is illustrated in Scheme 3. We assume the core region has been

Scheme 3. Assignment of Core Locants According to the Core Ring Scheme^a



^aThe core icosahedron of $\text{Au}_{25}(\text{SR})_{18}$ with principal C_5 axis is used as an example.

separated into different polyhedrons of atoms, the innermost polyhedron or atom is taken to be the central one, and we then carry out the following five steps:

(1) The core atoms in each polyhedron are sectioned into a set of parallel atomic planes that are perpendicular to the principal symmetry axis.

(2) Core atoms are then identified in each plane, and if there are more than three they are grouped into rings, by joining these coplanar core atoms to their nearest in-plane neighbors by bonds. In the case that there are only two atoms lying in a plane, then the same clockwise numbering scheme is used to number the atom on the right first and then the left.

(3) If there are central atoms or a central polyhedron, these are numbered separately and their locants are written as i , for a single central atom, and i_1, i_2, i_3 , etc., for the atoms of the central polyhedron. If the shape of the central polyhedron is not known a priori, once the core structure has been sectioned into rings, the central atoms may be identified with those that lie on inner concentric rings or isolated atoms at the center of a larger ring. Central atoms may also be identified in rings, or in isolated atoms, which lie on a plane that is sandwiched between neighboring planes above and below it that contain larger rings

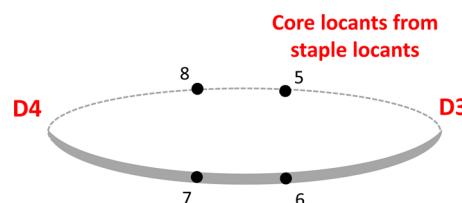
of core atoms, where the size of the ring is defined by its radial dimension.

(4) Numbering of the atoms of a polyhedral cluster in each plane is carried out in a circular manner, counting clockwise around the symmetry axis, and continuing through each of the parallel planes in sequence, from the first plane, which is at the top (or right), to the last plane, which is at the bottom (or left).

(5) In each plane, we give the lowest number to the atom in a ring that is on or just on the right of the 12 o' clock position (which is in the x' direction), viewing the ring down the symmetry axis from the top to the bottom.

2.4.3.2. Special Assignment Scheme: Core Locants from Staple Locants (for $\text{Au}_{25}(\text{SR})_{18}$). The core atoms are numbered in pairs according to the number of the staple to which they are bonded (see Scheme 4). Core atoms 1 and 2 are bonded to

Scheme 4. Core Locants Associated with the D3 and D4 Staples of the $C_2(y)$ Ring of $\text{Au}_{25}(\text{SR})_{18}$ ^a



^aThe staple atoms are not shown.

staple D1, core atoms 3 and 4 are bonded to staple D2, and in general staple D_n is bonded to core atoms $2n-1$ and $2n$. Core atoms that do not bond to the staples may be numbered in a sequence beginning after the last core atom that is associated with a staple. This scheme is suitable for the smaller aspicules, such as $\text{Au}_{25}(\text{SR})_{18}$, where staples bond to nearly all of the core atoms with the exception of the central one. In the case of aspicules with large cores, where there are many interior core atoms that do not bond to staples, it is best to apply the core ring locant scheme as we will demonstrate for $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$.

2.5. Aspicle Name Syntax. The third part of our nomenclature is naming, and we assemble a three-part name of the form below:

(Ligand Name)-Metal Name aspicle(charge)

The word “aspicle” indicates the family of molecules in an analogous way to the suffix fullerene in IUPAC fullerene nomenclature. The word aspicle is followed without a space by the electrical charge, which is written in parentheses as a final suffix to the name in accord with IUPAC nomenclature, for example, (−1), (+1), or (0), etc. Optionally, the compositional formula name of the counterion of the crystal structure may be specified in parentheses leaving a space after the charge. A further optional structural descriptor, in parentheses, may be specified after the charge or counterion formula, preceded by a space.

In aspicle names, we treat core and staple metal atoms equally and describe them using the single metal name. A hyphen is placed between the last ligand name and the metal name, and the only space in the name is left between the metal name and the suffix. If the ligand name is abbreviated using the $(\text{SR})_n$ notation, then a hyphen is placed between the last ligand name, or $(\text{SR})_n$, and the metal name:

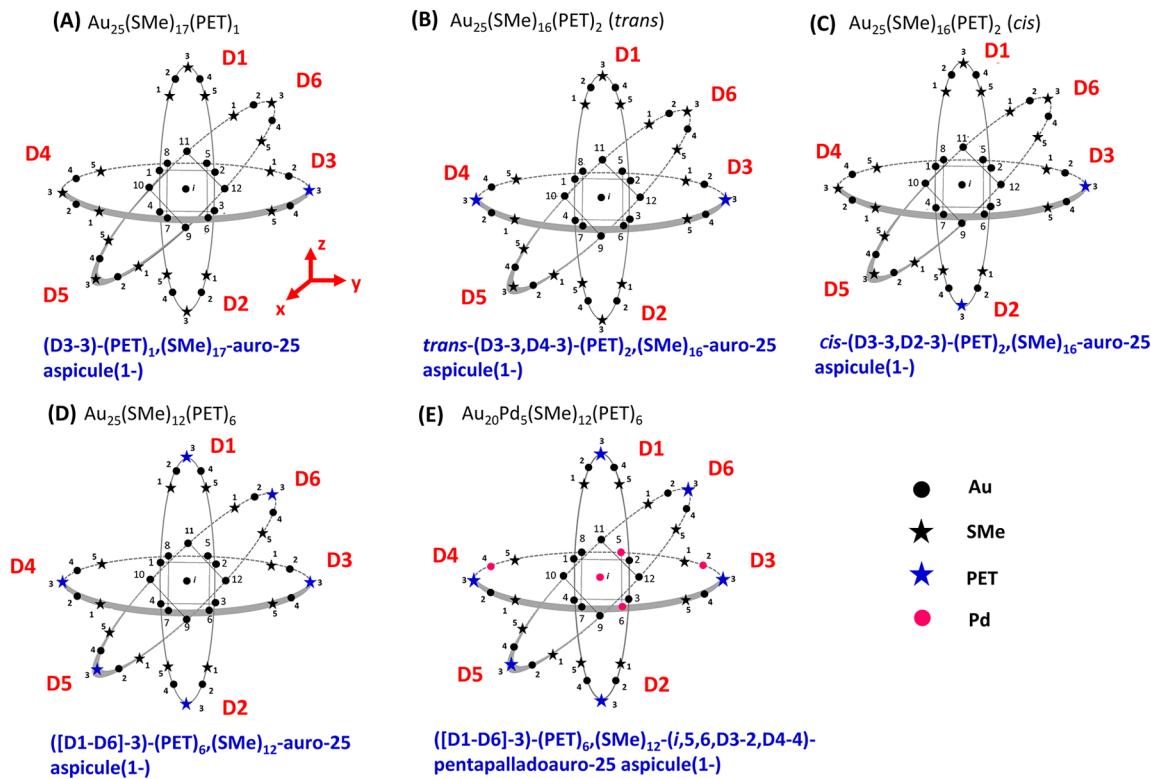


Figure 2. Modifications of $\text{Au}_{25}(\text{SMe})_{18}$ with ligand and metal atom substituents for the following cases: (A) a single bridging ligand (PET) exchange, (B) two bridging ligands exchanged in a *trans* configuration, (C) two bridging ligands exchanged in a *cis* configuration, (D) six bridging ligands exchanged, and (E) six bridging ligands and five metal (Pd) atoms exchanged (which is at present a hypothetical structure). For each example, the current formula name is shown above the diagram and its aspicule name is shown below. The atoms are colored and represented according to the legend, and the ligand (Me and PET) and metal atom type (Pd) are to be taken in a representative sense.

$(\text{SR})_n$ -Metal Name aspicule(charge)

For concreteness, we present as an example the name for $\text{Au}_{25}(\text{SMe})_{18}$ according to our nomenclature, which is 18-(methylthiolato)-auro-25 aspicule(1-) or $(\text{SMe})_{18}$ -auro-25 aspicule(1-), in its condensed form. The name for $\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$, based on the locants of Figure 1, which has two PET ligands exchanged at the bridging positions on the D1 and D2 staples, is (D1-3,D2-3)-di(2-phenylethane-thiolato),16(methylthiolato)-auro-25 aspicule(1-) or, in its condensed form, (D3-3,D4-3)-(PET)₂-(SMe)₁₆-auro-25 aspicule(1-). In this name, the locant prefix (D3-3,D4-3) denotes that the ligand exchange occurs at the two bridging sulfur atoms on opposite dimer staples in the *y*- and *y'*-directions, D3 and D4.

The rules of forming the ligand name and the metal name are formally described in sections 2.5.1 and 2.5.2. In section 2.5.5, we outline the stereodescriptor prefixes to the names.

2.5.1. Ligand Name. The following rules are observed in forming the ligand name of an aspicule:

2.5.1.1. Ligand Name and Number of Ligands. Ligand names may be specified, first, using the IUPAC nomenclature name of the ligand including its thiol group name, all enclosed in brackets. The number of ligands is specified using Greek multiplicative prefixes such as mono-, di-, tri-, etc., as in IUPAC nomenclature, or, as we introduce for brevity, a numerical multiplicative prefix. Thus, $(\text{PET})_2$ could be written as di(2-phenylethanethiolato), or as 2(2-phenylethanethiolato), where there is no space or hyphen between the prefix and the brackets around the ligand name.

2.5.1.2. Shorter Ligand Names. The second and more compact way of describing the ligands is using the $(\text{SR})_n$ terminology with an acronym for the R-group formed from its systematic name that is prefixed by the element symbol of the chalcogen atom, e.g. SG, or just the acronym of the R-group if it already includes an explicit reference to the thiol group, for example, (PET). In this terminology, the number of each type of ligand is written as a subscript outside the brackets. For brevity, we have chosen in certain places to present ligand names compactly by employing the $(\text{SR})_n$ terminology. If any of the ligands are chiral, the handedness is specified by prefixing a stereodescriptor from IUPAC organic nomenclature to the ligand name in its IUPAC form or before the S in the $(\text{SR})_n$ terminology name.

2.5.1.3. Order and Spacing of Ligand Names. The ordering of the ligand names and their prefixes is in the order of increasing number of the ligand, and a comma separates these different ligand names. A hyphen is used after the ligand names to separate them from the metal name following them.

2.5.1.4. Positions of Ligand Substituents. Each substituent ligand name is prefixed by its comma-separated locants in parentheses, followed by a hyphen to separate it from the ligand name, as in (D1-3,D1-5)-(PET)₂. The ordering of the ligand locants is, first, in the order of the staple number; for example, D1 always precedes D5, and then, second, in order of the positional number on the staple, for example, (D3-3,D3-5). No spaces are left after the commas separating the locants.

2.5.1.5. Example of a Name for $\text{Au}_{25}(\text{SR})_{18}$ with Ligand Substituents. An example of a name for $\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$, depicted in Figure 2B, which has two PET ligands substituted is

(D3-3,D4-3)-di(2-phenylethanethiolato),16(methylthiolato)-auro-25 aspicule(1-), or in its compact form (D3-3,D4-3)-(PET)₂,(SMe)₁₆-auro-25 aspicule(1-). The first part of this name (D3-3,D4-3)-(PET)₂,(SMe)₁₆ indicates that two Me ligand R-groups are substituted by PET ligand R-groups at precisely the D3-3 and D4-3 positions, which are bridging ligand positions on opposite staples. If there are substituents located at the same position on a series of staples, a contraction of the locants of a contiguous sequence of staple numbers is possible. We may condense this by specifying the first and last staples separated by a hyphen, all enclosed in square brackets, followed by the common position on each of the staples; for example, [D1–D6]-3 stands for (D1-3,D2-3,D3-3,D4-3,D5-3,D6-3).

2.5.2. Metal Name. The metal name contains the description of the metal atoms that are present in the core and the staples, and if there is more than one type of metal element, then the positions of the substituents are described using locant prefixes, in a way similar to ligand substituent prefixes.

The following rules are observed in forming the metal name of an aspicule:

2.5.2.1. Metal Element Names. Metal element names are of the form auro, pallado, and so on. These names are formed from the root word of the IUPAC Latin element names and adding an ending “o” to this root, for example, aur-o. We note that these names are also used elsewhere in IUPAC nomenclature for the “metallo” part of the names for metallocenes⁴⁷ (e.g., ferrocene) and metalloboranes (e.g., cobaltoborane). In the case that there is more than one type of metal element present, the metal name consists of minority metal element names being prepended to the majority metal element name, giving rise to compound names such as palladoauro, argentoauro, etc. It should be noted that these names have advantages of being unique and forming euphonic combinations, and hence are easy to remember.

2.5.2.2. Number of Metal Substituents. The number of metal atom substituents of a particular element is indicated by prepending the Greek multiplicative prefixes mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-, etc., to the substituent metal element name. Optionally, if there are a larger number of metal atom substituents, as might possibly be found in a larger aspicule such as Au₁₀₂(SR)₄₄, the number of substituents can be prefixed in Arabic numerals.

2.5.2.3. Positions of Metal Atom Substituents. The positions of metal atom substituents are described by prefixing their locants to the name of the respective substituent (minority) metal name within the compound metal name; for example, (i,2)-dipalladoauro represents substitution of the central atom and core atom 2. In the case of two minority metals, the locant prefix is inserted before the relevant name with a hyphen before it; for example, with Pd in positions 1 and 2 and Ag in positions 3 and 4, the compound metal name would be (1,2)-dipallado-(3,4)-diargentoauro-25. The ordering of the metal atom locants is to put the core locants first in numerical order, and then the staple metal atom locants.

2.5.2.4. Total Number of Metal Atoms. The total number of metal atoms that is characteristic of the structure is appended to the metal name as a final suffix, with a hyphen separating it from the metal name, for example, auro-25.

2.5.3. Example of a Name with Both Metal and Ligand Substituents. An example of a name for the six-ligand- and five-metal-atom-exchanged Au₂₀Pd₅(SMe)₁₂(PET)₆, shown in

Figure 2E, is ([D1–D6]-3)-hexa(2-phenylethanethiolato)-dodeca(methylthiolato)-(i,5,6,D3-2,D4-4)-pentapalladoauro-25 aspicule(1-) or, in its shorter form, ([D1–D6]-3)-(PET)₆,(SMe)₁₂-(i,5,6,D3-2,D4-4)-pentapalladoauro-25 aspicule(1-). The six ligands are exchanged at the bridging sulfur positions, and of the five Pd substitutions, three are in the core and two are in the staples.

2.5.4. Examples of Multimetallic Substituents. A five Pd atom-exchanged structure is certainly hypothetical at present, but we provide this example to show the potential scope of the nomenclature. Recently, trimetallic Au₂₅(SR)₁₈ aspicules have been synthesized.⁸⁴ Examples of hypothetical multimetallic Au₂₅(SR)₁₈ aspicules are the trimetallic Au₂₁Ag₂Pd₂(SMe)₁₈, which has two Pd atoms and two Ag atoms in the core, and could, for example, be named (SMe)₁₈-(i,1)-dipallado-(2,3)-diargentoauro-25 aspicule(1-), and the tetrametallic Au₁₈Ag₃Pd₂Pt₂(SMe)₁₈, one isomer of which might be named (SMe)₁₈-(i,2)-dipallado-(3,4)-diplatino-(5,6,7)-triargentoauro-25 aspicule(1-).

2.5.5. Stereodescriptors and Structure Descriptors.

2.5.5.1. Chirality Intrinsic to the Core and Staple Structure. The prefixes C and A used for intrinsic chirality are described in sections 2.9 and 2.10 on Au₃₈(SR)₂₄ and Au₁₀₂(SR)₄₄, which are aspicules that have chiral isomers. The chirality of organic ligand can be specified as a prefix to the ligand name following IUPAC organic nomenclature.

2.5.5.2. Geometric Isomerism of Ligands Bonded to the Same Staple. One descriptor of ligand configuration is the direction of the sulfur–carbon (S–C) bonds, which are described by additional prefixes (SI 7), and S–C bond directions are represented diagrammatically for Au₂₅(SR)₁₈ in Figure S7, which is based on the diagram of Figure 1. Because of the presence of a sulfur stereogenic center, the CIP priority and R/S system have been used for this purpose,²⁸ but we present an intuitive scheme based on the direction of the S–C bond with respect to the right-hand screw direction associated with a rotation following the sense of moving around the staple in order of increasing staple atom numbers. We note that for small high symmetry aspicules, each staple may be associated with the Cartesian axis that passes through the center of the core and the central atom of that staple. This provides a spatially intuitive alternative to using the staple locants (D1, D2, etc.), and this hybrid-directional locant scheme (SI 8) has been applied to Figure 1 (Figure S8).

2.5.5.3. Geometric Isomerism of Ligand and Metal Substituents on Different Staples. We observe in Figure 2B and C that concepts from stereochemistry and coordination chemistry such as *cis* and *trans* isomerism are applicable to ligand-exchanged isomers, because if we have substituted ligands at D3-3 and D4-3, it will be *trans*, while if the substitution occurs at D1-3 and D4-3, it would be *cis*. The *cis* and *trans* isomerism also applies to metal atom substituents. The prefixes *cis* and *trans* may be added to the beginning of an aspicule name or terminology to indicate the type of isomer followed by a hyphen between the aspicule name, or the terminology, for example, *cis*-Au₂₅(PET)₂(SMe)₁₆. A more accurate name involving ligand locants would be, for example, *cis*-(D2-3,D3-3)-(PET)₂,(SMe)₁₆-auro-25 aspicule(1-).

2.5.5.4. Internal Ligand Conformation and Ligand Chirality. Isomerism arising from changes in the ligand conformation of organic ligands (e.g., rotations about internal bonds) and the chirality of the ligand itself may be included as a

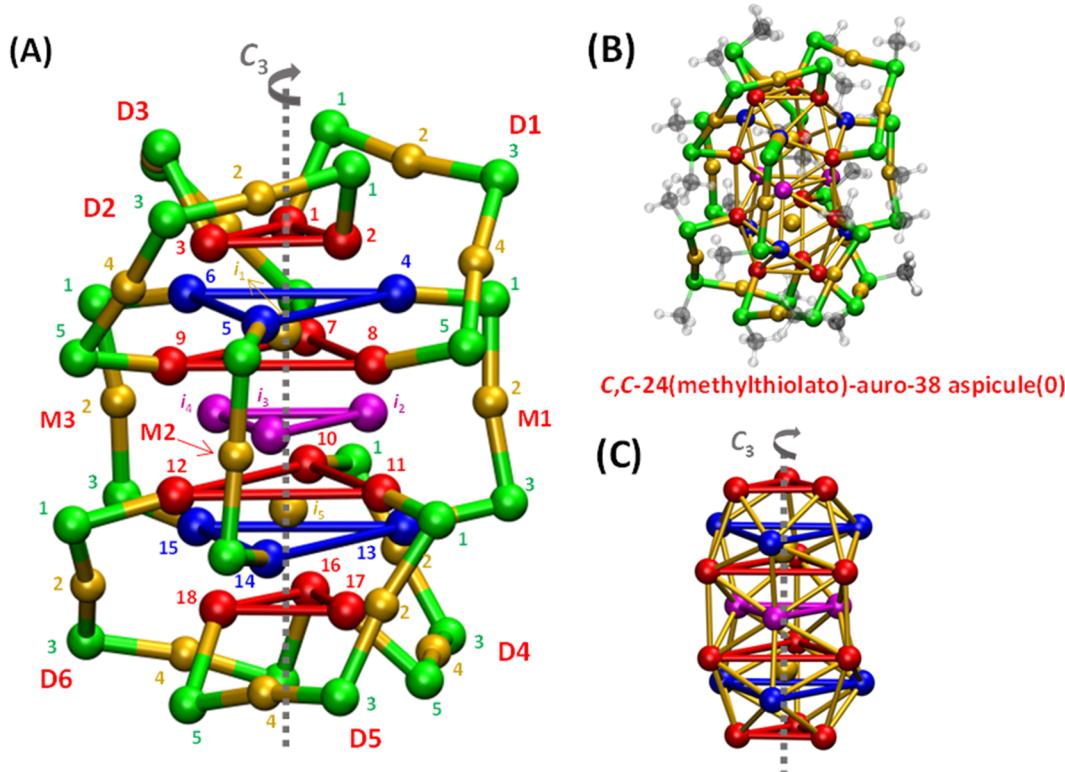


Figure 3. (A) The core and staple structure of $C\text{-Au}_{38}(\text{SMe})_{24}$ with the triangular rings of atoms lying in atomic planes perpendicular to the vertical C_3 axis (marked by the arrow at the top of the figure). The Au–Au bonds of the core have been omitted for clarity. The core atoms and the triangles are colored according to the type of staple they are located in (red for dimer staples and blue for monomer staples and magenta for the face sharing atoms of the bi-icosahedron). The staple and gold atoms at the center of the icosahedra are colored gold, while the sulfur atoms are colored green. Part (B) shows the complete structure of $\text{Au}_{38}(\text{SR})_{24}$ aspicule with Me ligand R-groups, and part (C) shows the bi-icosahedral core with the triangles of atoms in addition to Au–Au bonds. Triangles and the core atoms shown in (B) and (C) follow the same coloring scheme as in (A).

prefix and included as part of the ligand name, and described using terms such as trans and gauche(\pm).

2.5.5. Core Structure Descriptor and Staple Connectivity.

If there is another structural isomer with the same number of metal atoms but with a different core structure and symmetry, the distinction between the two aspicules can first be seen in the ligand name and number of ligands. We may also optionally add a descriptor describing the core polyhedral structure, after the charge, leaving a space. Structural descriptors for different core geometries may be found in SI 5. The main difference between the structural nomenclature and condensed nomenclature is that the staple connectivity to the core information must be included. The names are prefixed by the staple–core locant, which are of the form, for example, D1(1,2), which means that the staple D1 is bonded to core atoms 1 and 2. For $\text{Au}_{25}(\text{SR})_{18}$ in the topological representation with staple locants from the core locants, this connectivity information is actually contained in the staple locants, and the following locant sequence D1(1,2):D2(3,4):D3(5,6):D4(7,8):D5(9,10):D6(11,12) is prefixed to the front of the name to describe the staple–core connectivity of the parent aspicule. In the longer version of the names, the structure descriptor and the principal symmetry axis or axes must also be included. More precise syntax details on the structural nomenclature may be found in SI 5.

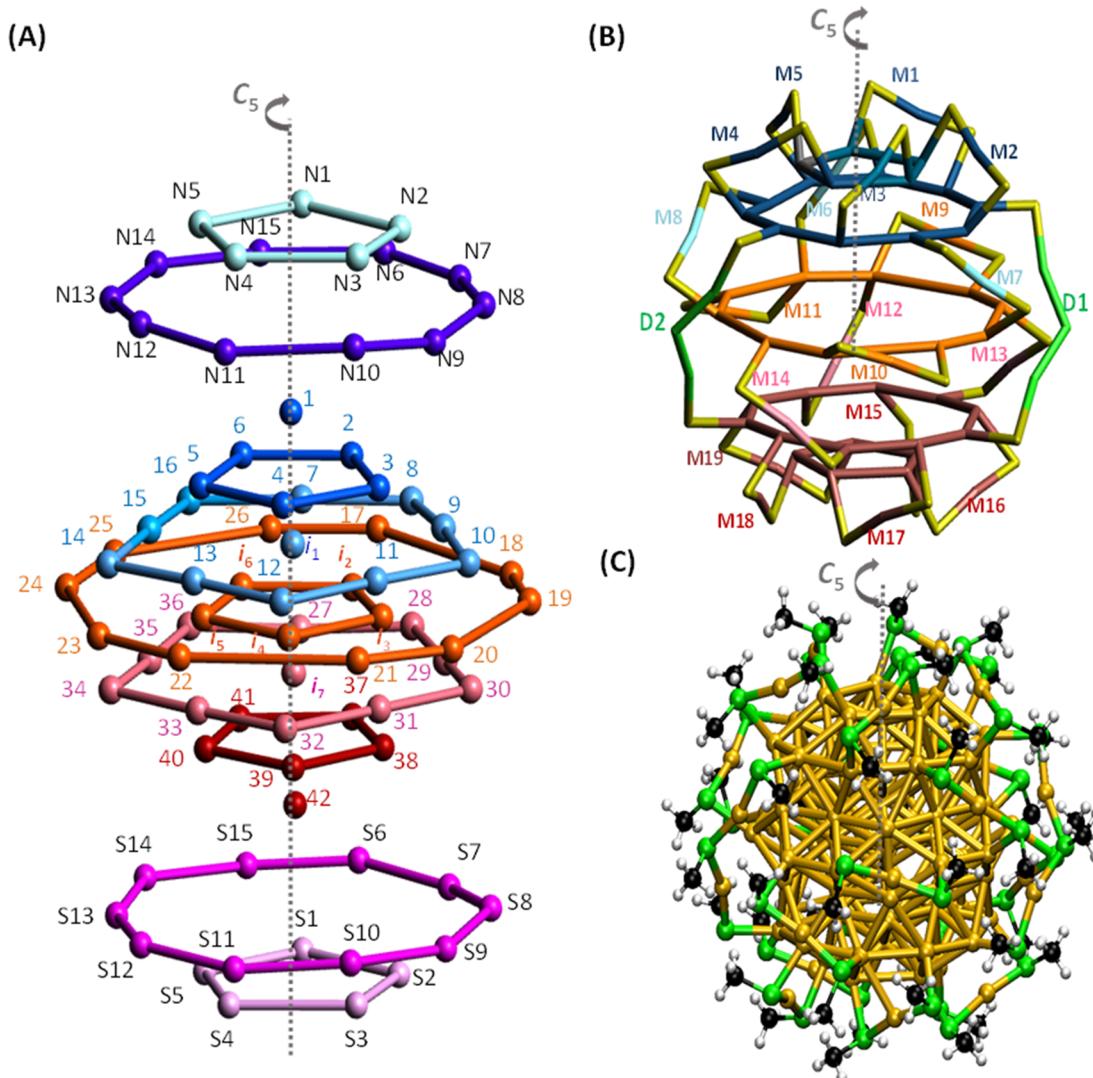
We can improve upon existing terminologies, such the formula name, $\text{Au}_{25}(\text{PET})_2(\text{SMe})_{16}$, by adding a prefix containing the locants of substituents to the relevant part of the formula name. For example, a two PET ligand substitution

of $\text{Au}_{25}(\text{SR})_{18}$ at the bridging positions of D1 and D2 staples would be $\text{Au}_{25}(\text{D}1\text{-}3,\text{D}2\text{-}3\text{-PET})_2(\text{SMe})_{16}$, where we have left out the second bracket around the locant prefix and also the first bracket around the ligand name. Several examples of terminologies for ligand and metal-atom-exchanged $\text{Au}_{25}(\text{SR})_{18}$ are shown in Tables S1 and S2 in SI 6.

We stress here that the nomenclature and terminologies described should only be applied to structures that have been determined through either X-ray diffraction or single-particle electron microscopy. A list of many of the known parent structures of $\text{Au}_M(\text{SR})_N$ and closely related structures containing silver, selenium, and chlorine, with their corresponding aspicule names, are given in Table S11 in SI 10.

2.6. Ligand and Metal-Atom Substituents in $\text{Au}_{25}(\text{SR})_{18}$. We considered various examples of ligand-exchanged and alloy modifications of $\text{Au}_{25}(\text{SR})_{18}$ and visualized the modifications using the diagram of Figure 1. Figure 2 shows several examples, including those mentioned earlier, for exchange of Me with a PET R-group for (A) a single bridging ligand, (B) two bridging ligands in a *trans* configuration, (C) two bridging ligands in a *cis* configuration, (D) six bridging ligands, and finally for (E) six bridging ligands and five Pd substituents.

Further examples of aspicule names with substituent positions for modified $\text{Au}_{25}(\text{SR})_{18}$ aspicules may be found in Tables S3 and S4 for different cases such as $\text{Au}_{25}(\text{SR})_{18}$ with six bridging ligand substitutions and one nonbridging ligand substitution, and two cases of metal-atom exchange with Pd



C-44(methylthiolato)-auro-102 aspicule(0)

Figure 4. (A) Core atoms of $C\text{-Au}_{102}(\text{SMe})_{44}$. The 49-atom Marks decahedron is shown at the center, and the two Au₁₅ "polar caps" are shown displaced slightly above and below the Marks decahedral core for clarity. The Au₇₉ gold core atoms have been divided into rings of atoms lying in planes perpendicular to the C_5 axis. The atoms and the edges of the rings that are shown by connecting "bonds" have both been colored uniquely according to the latitudinal position of the ring in which they lie with blues being used for rings in the Northern "hemisphere" and reds in the Southern "hemisphere", while the equatorial ring is shown in orange. (B) Staple structure of $C\text{-Au}_{102}(\text{SMe})_{44}$. The staples and those rings of core atoms that bond to the staples have been shown using the stick-bond representation, with their staple locants alongside. The staples are color coded in groups according to their position and size (as described in SI 12). Sulfur atoms on the monomer staples are shown in yellow and on dimer staples in green, while the color scheme for the gold atoms is described in the text. The staple-atom numbers on each of the staples have not been shown, but may be generated from this diagram and the core locants. (C) The complete structure of $C\text{-Au}_{102}(\text{SMe})_{44}$ with representative Me ligand R-groups is shown with its aspicule name in red below it. The gold, sulfur, carbon, and hydrogen atoms are colored gold, green, black, and white, respectively. Because of inherent structural irregularities in the mantle shell, the C_5 axis does not apply to the entire structure, including all of the staples, but only to the Au₁₅ polar caps, the M1–M5 and M15–M19 staples bonded to these polar caps, and the Marks decahedral core.

are also presented. Many of these cases have isomers (see below).

2.7. Isomers of Ligand and Metal-Atom-Exchanged $\text{Au}_{25}(\text{SR})_{18}$. We now consider examples of the structures and resulting names of geometric isomers of ligand and metal-atom-exchanged $\text{Au}_{25}(\text{SR})_{18}$. For the simplest case of a single ligand substitution, there are two symmetry-unique isomers, corresponding to exchange at either a bridging sulfur atom or a nonbridging sulfur atom, replacement of the central atom, a core surface metal atom, or an exterior (staple) metal atom. We now consider the case of substitutions of either two ligands or

two metal atoms: how many symmetry-unique isomers are there of each type, and what would be their structures and aspicule names? We used a method which takes into account the C_2 , C_3 , and chiral symmetry operations utilizing the diagram of Figure 1 to enumerate the number of symmetry-unique isomers, and this is described in SI 11. For two-ligand-exchanged $\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$, we counted 15 symmetry-unique isomers, and these are shown in Figure S9 in SI 11. In the case of alloying, we counted 28 symmetry-unique isomers for $\text{Au}_{23}\text{Pd}_2(\text{SMe})_{18}$, and we have depicted 18 of these in Figure S10 in SI 11 and provide a complete list of locants for all 28

isomers in Table S12 in SI 11. Examples of possible two metal-atom alloy isomers which involve only the core atoms are shown by visualization of their core icosahedron in Figure S11 in SI 12. The choice of Pd as the substituent is purely representative because it is known that Pd prefers to occupy the central site, while other metals such as silver do not.

2.8. $\text{Au}_{25}(\text{SR})_{18}$ Supramolecular and Conjugated Functionalization.

Aspicules whose ligands have either been functionalized or interact supramolecularly can be described by modifying the ligand name appropriately so that the ligand name where the interaction occurs and the type of interaction may be specified. Supramolecular interaction of Au_{25} with differing numbers of β -cyclodextrin molecules gives rise to $\text{Au}_{25}(\text{BBSH})_{18-n}(\text{BBSH}\cap\text{CD})_n$ adducts, and these aspicules can be named as shown in Table S5. For the four β -cyclodextrin (CD)-attached $\text{Au}_{25}(\text{BBSH})_{14}(\text{BBSH}\cap\text{CD})_4$ supramolecular adduct, we have used the positions of Mathew et al.¹⁰⁰

Fluorescein isothiocyanate (FITC) molecules interact with the amine group of the dansyl glutathione (SDG) ligands of $\text{Au}_{25}(\text{SDG})_{18}$ ¹⁰¹ to form $\text{Au}_{25}(\text{SDG})_{18-n}(\text{SDG-FITC})_n$ adducts, and names for adducts with between one and four FITC molecules are given Table S6. We remark that the above systems are given as examples because their precise structures have not yet been determined experimentally.

2.9. $\text{Au}_{38}(\text{SR})_{24}$. In this section and the next, we describe how we obtained tomographic ring representations of the core and staples of two highly stable aspicules with crystal structures, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$. The tomographic sectioning is more straightforward to carry out than finding the rings containing both the core and the staple atoms as we did for $\text{Au}_{25}(\text{SR})_{18}$; hence, we opted for this kind of representation. The structural insights derived from these representations are outlined in section 2.11, and we also label our diagrams with locants so that modifications can be identified. The core structure of $\text{Au}_{38}(\text{SR})_{24}$ consists of a face-fused bi-icosahedron with two central atoms and six dimer staples, which are arranged in two groups of three staples twisting around the C_3 axis at either end of the bi-icosahedron, and the point group is pseudo D_{3h} .^{51,102} We have used the structure of Qian et al.⁴⁰ for visualization and analysis, and Figure 3B shows this structure with Me ligand R-groups, and also with the core atoms colored according to which plane perpendicular to the C_3 axis they lie in and their bonding environment.

The bi-icosahedral core is sectioned into seven triangles (three-membered rings) located in parallel planes lying perpendicular to the C_3 axis, as shown in Figure 3C. Each triangle of core atoms is colored blue or red according to whether the atoms are bonded to monomer or dimer staple atoms, respectively. The central triangle, shown in magenta of face-sharing atoms, may be grouped with the two central gold atoms to constitute a central trigonal bipyramidal whose atoms may be labeled i_1-i_5 . The numbering of the remaining core atoms proceeds from the top red triangle to the bottom red triangle according to the core ring locant scheme.

Figure 3A shows the core and staple structure of $\text{Au}_{38}(\text{SR})_{24}$ with locants. The dimer staples, D1, D2, and D3, are counted in a clockwise manner ($\text{D1} \rightarrow \text{D2} \rightarrow \text{D3}$) around the C_3 axis. We count the staple closest and to the right of the x' direction going into the paper, because it coincides with the direction of the 12 o' clock position looking down the C_3 axis from the top. This procedure is repeated for the other three dimer staples at the bottom end, D4, D5, and D6, and finally the three centrally located monomer staples are numbered as M1, M2, and M3.

We note that there is already a terminology for chiral and achiral isomers of $\text{Au}_{38}(\text{SR})_{24}$ introduced by Knoppe et al.,¹⁰³ based on IUPAC stereochemical nomenclature of coordination compounds: A,A- $\text{Au}_{38}(\text{SR})_{24}$, C,C- $\text{Au}_{38}(\text{SR})_{24}$, and the achiral A,C- $\text{Au}_{38}(\text{SR})_{24}$ isomer, where A and C stand for anticlockwise and clockwise. A single prefix, A or C, may be used if all of the staples "rotate" in the same direction, as appropriate.

In Figure 3A, if we look down the C_3 axis from above, we see that core atom 4 bonded to the lower end of the D1 staple, located in the third triangle from the top, is found in a clockwise direction around the symmetry axis with respect to core atom 1 bonded to the upper end of the staple. This direction of rotation is also the case for the other two staples D2 and D3.^{28,104} A similar scenario is found for D4, D5, and D6, if we now look upward from the bottom of the C_3 axis. Thus, the staples in this enantiomer are considered to be rotating clockwise and have C or right-handed chirality. The structure shown in Figure 3 is the chiral C,C- $\text{Au}_{38}(\text{SR})_{24}$ or C-Au₃₈(SR)₂₄ isomer in this notation.

An example of a name for the parent structure of $\text{Au}_{38}(\text{SR})_{24}$ is C,C-24(methylthiolato)-auro-38 aspicule(0), and this would shorten to C-(SMe)₂₄-auro-38 aspicule(0). One example with four ligand substitutions in the bridging positions of two dimer and two monomer staples, and with two central Pd atoms, is C-(D1-3,D2-3,M1-1,M2-3)-(PET)₄-(SMe)₂₀-(i_1,i_5)-dipalladoauro-38 aspicule(0), or C-(D1-3,D2-3,M1-1,M2-3)-tetra(2-phenylethanethiolato),20(methylthiolato)-(i_1,i_5)-dipalladoauro-38 aspicule(0).

2.10. $\text{Au}_{102}(\text{SR})_{44}$. We apply our structural analysis to $\text{Au}_{102}(p\text{-MBA})_{44}$, or equivalently $\text{Au}_{102}(\text{SMe})_{44}$, which was the first aspicule to have its crystal structure determined, and a visualization of the right-handed enantiomer C- $\text{Au}_{102}(\text{SMe})_{44}$ can be seen in Figure 4C. $\text{Au}_{102}(\text{SR})_{44}$ has 89 gold atoms that have pseudo D_{5h} symmetry, apart from the 13 irregularly located ones in the staples around the equatorial region.^{48,105} We used the structure of C- $\text{Au}_{102}(\text{SR})_{44}$ from Jung et al.¹⁰⁶ for visualization. We select as the principal symmetry axis the C_5 axis passing through the center of the 49-atom Marks decahedron (MD_{49}) located in the inner-core region, and rotate the structure into a standard orientation, as described in SI 13 and shown in Figure 4C. The 10 monomer staples bonded to the "polar caps" also exhibit C_5 symmetry, but the two dimer staples and the remaining nine monomer staples do not; however, this does not affect the choice of the C_5 principal axis.

The three regions of N and S Au_{15} polar caps, where N (north) and S (south) distinguish the upper and lower fragments, and the outer shell of the Marks decahedron and its central pentagonal bipyramid are numbered in separate groups following the core ring locant procedure, and the result is shown in Figure 4A. Because of the equatorial C_2 symmetry plane, we numbered the south polar Au_{15} fragment starting from the southernmost ring, rather than the one above it.

The staple locant assignment, shown in Figure 4B, is carried out in six groups, with each group consisting of a set of staples of similar size and latitudinal position. The staples in each group are counted clockwise around the C_5 axis, beginning from the northernmost monomer staple group, proceeding downward through each group in turn until the southernmost monomer staple group and then counting the two dimer staples in the final group. Further details of the standard orientation, locant assignment, the staple groups, and color scheme of Figure 4B are given in SI 13. The staple–core connectivity is

shown in Figure S12 in SI 13, which is similar to Figure 4B, but with the locants for core atoms in the outer shell being shown.

We have not shown the locants for the ligands and the staple metal atoms in Figure 4B, but these may be ascertained by assigning the staple atom numbers to each staple following the schemes in section 2.4.2.1. The parent structure of $\text{Au}_{102}(\text{SMe})_{44}$ can be named immediately as 44-(methylthiolato)-auro-102 aspicule(0) or auro-102 aspicule(0), the latter being the mirror image of the structure of Figure 4C. An example of a modification is the name of one isomer of $\text{C-Au}_{102}(\text{SMe})_{40}(\text{PET})_4$, which has four PET ligands substituted on four monomer staples. The substituent locations are on two different staples bonded to the north polar cap, and on two other staples: one in the northern hemisphere and one in the equatorial staple group. This would be named as C-(M1-1,M2-3,M7-1,M10-3)-tetra(2-phenylethanethiolato),40-(methylthiolato)-auro-102 aspicule(0), or, more compactly, C-(M1-1,M2-3,M7-1,M10-3)-(PET)₄(SMe)₄₀-auro-102 aspicule(0). A comparison of aspicule names for $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, and $\text{Au}_{102}(\text{SR})_{44}$ with a single modification is given in Table S8, while names for these aspicules, which include more structural information, are shown in Tables S9 and S10, and the latter table presents names that include complete staple connectivity to the core. An extension to other multishell core clusters of other metals, such as $(\mu_{12}\text{-Pt})\text{Pd}_{164-x}\text{Pt}_x(\text{CO})_{72}(\text{PPh}_3)_{20}$ ($x \sim 7$) of ref 88, which has both terminal ligands on the surface of the core and intershell bridging ligands inside the core, is possible by assigning its locants following a procedure similar to $\text{Au}_{102}(\text{SR})_{44}$. Because there are no staples, we use ligand locants beginning with the letters μ and C, to denote bridging or terminal sulfur atoms. A basic example of a name with locants for the Pt positions would be $(\text{CO})_{72}(\text{PPh}_3)_{20}\text{-}(i,1,2,3,4,5,6,7)\text{-octaplatinopallado-165}$ aspicule(0). The specific locants for the eight Pt atoms are given as an example and are not based upon the structure, apart from the central one. Further prefixes may be inserted specifying ligand positions for modifications or structural descriptors if greater structural detail is required.

2.11. Structural Insights. First and foremost, the identification of a topologically interesting configuration such as the Borromean rings is a very significant but hitherto unrecognized finding in the context of understanding the structure of $\text{Au}_{25}(\text{SR})_{18}$ but also, perhaps, that of the structures of gold thiolate aspicules in general. This is the most important example of an interlocked ring configuration found for an aspicule, which has a known crystal structure, the others being $\text{Au}_{10}(\text{SR})_{10}$ ¹⁰⁷ which is a catenane, and $\text{Au}_{20}(\text{SR})_{16}$ ¹⁰⁸

These two examples suggest that rings and topological linking or interlocking of rings may be a more general feature of part of the inner bonding network of aspicules, and represent a unified view of this part of the structure involving both core and staple atoms, rather than the division between the core and the staples.

A physical distinction of these rings may be seen in the differences found in the lengths of the Au–Au core bonds (colored red, blue, and green in inset (i) of Figure 1), which lie in the (Au_8S_6) -rings, being all of same length ($\sim 2.79 \text{ \AA}$) and slightly shorter⁷¹ than the other Au–Au bonds in the icosahedron ($\sim 2.99 \text{ \AA}$) (colored gold in Figure 1, inset (i)), apart from the bonds to the central atom, which are also of length similar to those in the rings.⁷¹ The geometric stability arising from the greater depth of the energy minimum at the ground-state geometry of $\text{Au}_{25}(\text{SR})_{18}$ may be in part related to

the shorter⁷¹ and therefore stronger bonds in the rings and to the triple-interlocking of the rings around the central atom, which provides a strong framework for the whole molecule.

The second structural viewpoint was the tomographic one, where parallel rings of core atoms and staples winding around a common symmetry axis are found, which might also be generally applicable to many more aspicules. The bonds between core atoms lying on adjacent rings have been left out, which clearly shows the parallel sets of atomic rings, or planes containing single atoms, in the core region and with different groups of staples joining different rings together. We use the term ring in the sense of the connectivity, because the atoms in these rings actually lie in triangles or other polygons (e.g., as shown in Figures 3A and 4A). We may distinguish three types of rings depending on whether all of the atoms in the ring are bonded to each other (e.g., the triangle with atoms 1, 2, and 3 of Figure 3A), some are bonded to each other and some not (e.g., the atoms in the orange equatorial ring in Figure 4A), and last, none of the atoms in the ring are bonded. The latter case occurs if all of the atoms are separated by at least next nearest-neighbor bond distances (e.g., the triangle with atoms 4, 5, 6 in Figure 3A). The core atom ring configurations shown in Figures 3A and 4A suggest a mechanism by which the core forms by stacking (or growth) of ring configurations (with or without intraring bonds) of gold atoms, above and below a central polyhedron or central atom in $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$. From this representation, we cannot, however, conclusively identify the precise structural units that lead to this formation. One further significance of these core rings is that the preferential sites of Ag alloy substituents in $\text{Au}_{38}(\text{SR})_{24}$, for example, lie in these rings.⁵⁵ The smaller triangles at the top, center, and bottom of $\text{Au}_{38}(\text{SR})_{24}$ in Figure 3A are precisely those that are preferred for Ag atom alloying. A slight preference for opposite triangles of Ag atoms lying perpendicular to the C_3 axis in Ag doping of $\text{Au}_{25}(\text{SR})_{18}$ has also been observed.⁵⁷

Third, a detailed understanding of the structure of isomers was obtained through the enumeration and naming of the cases of two ligand or two-metal atom substituents for $\text{Au}_{25}(\text{SR})_{18}$. Here, we took into account symmetry equivalence and chirality, and diagrammatically represented the structures of chiral isomers and *cis-trans* analogue isomers.

Finally, we note that a set of symmetry-equivalent sites would only be equivalent with respect to the metal or sulfur atom site positions, but not with respect to the metal or ligand atoms associated with those sites once a modification has broken the symmetry. Hence, the locant system we have presented provides a unique label for each metal atom or ligand and is a more general and precise system for specifying substituent positions.

3. SUMMARY

We carried out a structural simplification of the highly stable $\text{Au}_{25}(\text{SR})_{18}$ and identified within the bonding network the topological configuration consisting of interlocked Au_8S_6 (Borromean) rings, which provides a unified structural viewpoint including both core and staple atoms, and which forms a strongly bonded framework that is possibly responsible for the high geometric stability of this molecule. The Borromean rings diagram of $\text{Au}_{25}(\text{SR})_{18}$ was also used to represent its various modifications, such as ligand-exchange, alloying, and functionalization (supramolecular/conjugated interaction). We also incorporated our methods of structural

analysis into a structure-based nomenclature, including positionally precise terminologies, for gold thiolate aspicules that is symmetry-based, provides a complete framework to describe and understand the structural diversity of $\text{Au}_M(\text{SR})_N$ and $\text{Au}_M(\text{X})_N$ and is adaptable to the general case of $\text{M}_M(\text{X})_N$ with additional modifications to account for any atypical structural features that may be encountered.

Developing simplified structural representations of gold thiolate aspicules of different sizes, both smaller than $\text{Au}_{25}(\text{SR})_{18}$ (e.g., $\text{Au}_{15}(\text{SR})_{13}^{91}$ and $\text{Au}_{18}(\text{SR})_{14}^{109}$) and also larger (e.g., $\text{Au}_{133}(\text{SR})_{52}^{54,60}$ and $\text{Au}_{144}(\text{SR})_{60}^{111,112}$) with coordinating atoms other than sulfur, and also of aspicules with different predominant metals such as silver, for example, $\text{Ag}_{44}(\text{SR})_{30}^{62,63}$ is the subject of ongoing and further work. Because chirality is found in nearly all aspicules, it is necessary to produce simplified diagrams for each of the enantiomers. Finding symmetry-equivalent isomer structures for the general cases of isomers with n substituent ligands/metal atoms is another possible direction. Finally, we wish to emphasize that this Article is not about the name aspicule for this class of molecules, which may be decided by a consensus of workers in the field, but is focused on understanding the structure and modifications within a unified framework.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcc.5b08193](https://doi.org/10.1021/acs.jpcc.5b08193).

Additional data and systematic instructions for drawing the Borromean rings diagram of $\text{Au}_{25}(\text{SR})_{18}$ ([PDF](#))

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Author Contributions

G.N. and T.P. carried out structural analysis and developed the nomenclature. G.N., A.M., and T.P. wrote this Article. A.M. also contributed to the production of the figures. Y.N. and R.L. reviewed and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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