New insight into the electronic shell of Au\textsubscript{38}(SR)\textsubscript{24}: a superatomic molecule†

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Based on the recently proposed super valence bond model, in which superatoms can compose superatomic molecules by sharing valence pairs and nuclei for shell closure, the 23c-14e bi-icosahedral Au\textsubscript{23}(SR)\textsubscript{24} core of Au\textsubscript{38}(SR)\textsubscript{24} is proved to be a superatomic molecule. Molecular orbital analysis reveals that the Au\textsubscript{23}(SR)\textsubscript{24} is an exact analogue of the F\textsubscript{2} molecule in electronic configuration. Chemical bonding analysis by the adaptive natural density partitioning method confirms the superatomic molecule bonding framework of Au\textsubscript{38}(SR)\textsubscript{24} in a straightforward manner.

Thiolate-protected gold (Au-SR) nanoparticles with core diameter of 0.5–2 nm are of significant interest due to their distinct electronic transition in optical absorption, intrinsic magnetism, enhanced photoluminescence, discontinuous charge transport and redox properties, and applications in catalysis. 3

Crystallization and structural determination of Au\textsubscript{102}(SR)\textsubscript{44} was a breakthrough in nanogold research. 2 The seminal X-ray crystal structure determination showed that the thiolate ligands do not simply passivate a large gold core but instead form Au\textsubscript{n}(SR)\textsubscript{2n+1} (n = 1, 2) oligomers that bind to a smaller gold core. This packing agrees with the previous “divide-and-protect” model 1 in concept. The 44 thiol groups of Au\textsubscript{102}(SR)\textsubscript{44} form 21 staple motifs 4 on the surface, 19 Au(SR)\textsubscript{2} and 2 Au\textsubscript{2}(SR)\textsubscript{3} units. Later, the Au\textsubscript{25}(SR)\textsubscript{18} units were also observed in the crystal structure of Au\textsubscript{58}(SR)\textsubscript{18}. 5 Knowledge of the binding motifs of Au\textsubscript{23}(SR)\textsubscript{18} has been obtained from density functional theory (DFT) predictions 6 independent of and in agreement with X-ray crystal structure determination. DFT 7 and X-ray 8 investigations of Au\textsubscript{18}(SR)\textsubscript{24} have revealed that these motifs are ubiquitous. Moreover, based on the model of a gold core surrounded by gold thiolate oligomers, DFT calculations have been used to predict the structures of Au\textsubscript{10}(SR)\textsubscript{5}, Au\textsubscript{22}(SR)\textsubscript{5}, Au\textsubscript{20}(SR)\textsubscript{16}, Au\textsubscript{34}(SR)\textsubscript{20}, Au\textsubscript{44}(SR)\textsubscript{28}, and Au\textsubscript{44}(SR)\textsubscript{20}, which have not yet been determined by experiments. All of these clusters have molecule-like electronic structures in which the highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gap can be correlated to measured optical and electrochemical values.

Electronic shell closure based on the jellium model has successfully explained the observed experimental abundances of alkali-metal clusters in the gas phase. 13 The spherical jellium model assumes a uniform background of positive charge of the cluster’s atomic nuclei and the innermost electrons, in which valence electrons move and are subjected to an external potential. To explain the electronic stability of Au-SR nanoparticles, Hakkinen et al. 16 extended the superatom model to treat Au-SR nanoparticles by accounting for ligand interactions with the nanoparticle core. The electron count of the Au\textsubscript{n}(SR)\textsubscript{m} compound is determined as n* = N - M - z, where N and M are related to the cluster stoichiometry, and z is the charge state of the compound. The appropriate Aufbau rule of delocalized “superatomic orbitals” of Au clusters is |1S\textsuperscript{2}|1P\textsuperscript{6}|1D\textsuperscript{10}|2S\textsuperscript{2}1F\textsuperscript{14}| 2P\textsuperscript{6}1G\textsuperscript{18}|2D\textsuperscript{10}3S\textsuperscript{2}1H\textsuperscript{22}| [...], and exceptional stability is associated with the magic numbers (n* = 2, 8, 18, 34, 58, 92, ...). Superatom theory has achieved great success in Au-SR nanoparticles, of which the stability of many clusters can be understood with the magic numbers, such as Au\textsubscript{102}(SR)\textsubscript{44} (n* = 58), Au\textsubscript{68}(SR)\textsubscript{34} (n* = 34), Au\textsubscript{44}(SR)\textsubscript{28} (n* = 18), Au\textsubscript{25}(SR)\textsubscript{18} (n* = 8), and Au\textsubscript{12}(SR)\textsubscript{6} (n* = 2). 10

Besides the electronic shell closure based on the superatom model, geometric shell closure is also very important for Au-SR clusters. Among the ligand-protected gold nanoparticles with a superatom core, Au\textsubscript{23}(SR)\textsubscript{18} is most interesting in both electronic and geometric shell closure, which has a nearly idealized icosahedral core of Au\textsubscript{13}, where twelve vertexes of the icosahedron are stapled by six Au\textsubscript{3}(SR)\textsubscript{2} oligomers. The icosahedral core...
is a 13-center 8-electron (13c-8e) superatom. Electronic structures of \( \text{Au}_{23}(\text{SR})_{18} \) are consistent with the superatom model, in which the large HOMO–LUMO gap (\(~1.3\) eV) can be viewed as P–D superatom orbitals.\(^{18}\)

The superatom model can treat only those clusters with a spherical core, and the stability of clusters with a non-spherical core, such as \( \text{Au}_{138}(\text{SR})_{24} \),\(^*\) cannot be understood. As shown in Fig. 1a, \( \text{Au}_{138}(\text{SR})_{24} \) also has a magic geometric shell, which has a face-fused bi-icosahedral \( \text{Au}_{23} \) core. Eighteen vertexes of the bi-icosahedron are stapled by six \( \text{Au}_{3}(\text{SR})_{3} \) and three \( \text{Au}(\text{SR})_{2} \) oligomers, of which each oligomer withdraws one electron and there are 14 valence electrons delocalized in the \( \text{Au}_{23} \) core (Fig. 1b). \( \text{Au}_{138}(\text{SR})_{24} \) has a sizable HOMO–LUMO gap (\(~0.9\) eV) and a large adiabatic ionization potential,\(^{27}\) indicating a high electronic stability. However, the 14 valence electrons delocalized in the bi-icosahedral \( \text{Au}_{23} \) core disagree with the count in the superatom model. The electronic stability of \( \text{Au}_{138}(\text{SR})_{24} \) has been explained by Aikens et al.\(^{28}\) using the parameter-based particle-in-a-cylinder model, a variation of Clemenger’s ellipsoidal shell model,\(^{29}\) with certain parameters. The parameters give no direct physical picture, and the model is entirely structureless.

Recently, we proposed a super valence bond (SVB) model\(^{26}\) to explain the electronic stability of non-spherical shells of metal clusters, and found that \( \text{Li}_{8}, \text{Li}_{10}, \text{Li}_{14} \) are exact analogues of \( \text{CH}_{4}, \text{N}_{2}, \text{F}_{2} \), respectively, in electronic state and bonding patterns. Note that the \( \text{Au}_{23} \) core of \( \text{Au}_{138}(\text{SR})_{24} \) is a union of two 13c-7e icosahedral units and has 14 valence electrons, of which a three-nucleus triangle face is shared by the two 13c-7e icosahedral units and has 14 valence electrons, of which each oligomer withdraws one electron and there are 14 valence electrons delocalized in the \( \text{Au}_{23} \) core (Fig. 1b). \( \text{Au}_{138}(\text{SR})_{24} \) has a sizable HOMO–LUMO gap (\(~0.9\) eV) and a large adiabatic ionization potential,\(^{27}\) indicating a high electronic stability. However, the 14 valence electrons delocalized in the bi-icosahedral \( \text{Au}_{23} \) core disagree with the count in the superatom model. The electronic stability of \( \text{Au}_{138}(\text{SR})_{24} \) has been explained by Aikens et al.\(^{28}\) using the parameter-based particle-in-a-cylinder model, a variation of Clemenger’s ellipsoidal shell model,\(^{29}\) with certain parameters. The parameters give no direct physical picture, and the model is entirely structureless.

To verify such a supposition on the chemical bonding of \( \text{Au}_{138}(\text{SR})_{24} \), we first studied the electronic structure of the \( \text{Au}_{23} \) core of \( \text{Au}_{138}(\text{SR})_{24} \) for simplicity and clarity. Based on the SVB model, \( \text{Au}_{23} \) can be seen as an analogue of \( \text{F}_{2} \) in chemical bonding. To verify this point of view, Fig. 2a compares their canonical Kohn–Sham molecular orbital (MO) diagrams of the valence shell. Chemical bonding of \( \text{F}_{2} \) is a classical case of valence bond (VB) theory in textbooks, in which there are three lone pairs in each F and one covalent pair shared by two F. In the canonical MO of \( \text{F}_{2} \), the two s atomic orbitals (AOs) are split into two sets (\( \sigma_{s} \) and \( \sigma^{*} \)), the four \( \pi \) and \( \pi^{*} \) AOs are split into two doubly degenerate sets (\( \pi_{p,p}, \pi^{*} \)), and the p AO is also split into two sets (\( \sigma_{p} \) and \( \sigma^{*} \)). The electronic configuration is \( \sigma_{s}^{2} \sigma^{*}_{s}^{2} \pi_{p,p}^{4} \pi^{*}_{p,p}^{4} \sigma^{*}_{p}^{2} \). To our surprise, the canonical MO diagrams of \( \text{Au}_{23} \) are obviously analogous of those of \( \text{F}_{2} \) both in MO shapes and orders (except for the order of \( \sigma_{p} \) and \( \pi_{p,p} \)). The 23c-14e bi-icosahedral core can be taken as a superatomic molecule bonded by two 7-electron superatoms, of which two electrons are shared by the two superatoms for 8-electron shell closure each. It is noted that here we focused only on the comparison of the valence shells of \( \text{Au}_{23} \) and \( \text{F}_{2} \). If one includes inner and/or outer shells, there will be both similarities and dissimilarities between the atomic and superatomic shells. For example, \( \text{Al}_{13} \) is a well known super-halogen, but the electronic configuration of \( \text{Al}_{13} \) is of course different from that of \( \text{Br} \).
Next, to give a direct view on the chemical bonding of a cluster, we selected the adaptive natural density partitioning (AdNDP) method as a tool for chemical bonding analysis. This method was recently developed by Zubarev and Boldyrev\textsuperscript{21} and used to analyze chemical bonding in organic molecules, boron clusters, and Au clusters.\textsuperscript{22} AdNDP recovers both Lewis bonding elements (1c-2e and 2c-2e objects) and delocalized bonding elements (nc-2e), which achieves seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance. The 8e-superatom model of Au\textsubscript{23}(SR)\textsubscript{18}\textsuperscript{−} is successfully confirmed by AdNDP analysis, and direct evidence for the delocalized superatomic orbitals (S\textsuperscript{2p\textsuperscript{6}}) is given (see Fig. S1 in ESI!).

Chemical bonding analysis by AdNDP confirms further the superatomic molecule model of Au\textsubscript{23}\textsuperscript{(+9)}. As shown in Fig. 2b, AdNDP analysis reveals three 13c-2e super lone pairs (LPs) (super S, P\textsubscript{a}, and P\textsubscript{b}) in each 13c-superatom, and one 23c-2e super σ-bond in the Au\textsubscript{23}\textsuperscript{(+9)} cluster. The Au(5d) orbitals are viewed as LPs with ON = 1.86–1.98[e], and are not plotted in this figure. Such a bonding framework shows clearly that the Au\textsubscript{23}\textsuperscript{(+9)} cluster can be viewed as a superatomic molecule bonded by two 13c-7e superatoms, of which two electrons and three nuclei are shared by the two superatoms.

Ligand effects are also very important for Au-SR clusters. Lastly, we carried out a total bonding analysis of Au\textsubscript{38}(SR)\textsubscript{24} using AdNDP. The R groups do not affect much of the overall bonding patterns of the compound, thus we used SH instead of SR for simplicity and clarity in the chemical bonding analysis. Fig. 3 plots the bonding framework of the valence shells of Au\textsubscript{38}(SH)\textsubscript{24} from AdNDP analysis. As expected, the Au(5d) orbitals are viewed as LPs with ON = 1.86–1.98[e], which are excluded in this analysis. AdNDP analysis reveals 24 LPs of S atoms with ON = 1.94–1.95[e], 24 2c-2e localized SH σ-bonds with ON = 1.98–1.99[e], and 48 2c-2e localized AuS σ-bonds with ON = 1.90–1.93[e]. The remaining 14 electrons are delocalized in the Au\textsubscript{23} bi-icosahedral core: two s-type 13c-2e super-LPs, four p-type 13c-2e super-LPs, and one 23c-2e super-σ. The bonding analysis confirms that the Au\textsubscript{23} core of Au\textsubscript{38}(SR)\textsubscript{24} is a superatomic molecule in electronic structure.

In summary, based on the SVB model, the 23c-14e double-icosahedral Au\textsubscript{23}\textsuperscript{(+9)} core of Au\textsubscript{38}(SR)\textsubscript{24} is an exact analogue of the F\textsubscript{2} molecule in both MO diagrams and bonding patterns, of which electronic shell closure is obtained beyond the magic numbers of superatoms. Superatom theory has achieved great success in ligand-protected Au nanoparticles. However, the SVB model gives new physical insight into the shell closure of delocalized electrons, and extends the superatom model. Geometric shell closure is as important as electronic shell closure, and unusual stability requires both geometric and electronic shell closure in Au-SR clusters. Although the superatomic molecule shell may be less stable than the superatom shell, it is more diverse and flexible in matching the geometric shell. We believe that such an electronic shell closure of a superatomic molecule may exist in some other ligand-protected Au nanoparticles, and the SVB model is helpful in guessing the structure of some other Au-SR clusters which are isolated but not yet crystallized. For example, in a recent surfactant-free synthesis of small Au-SR clusters,\textsuperscript{23} some 10e compounds (Au\textsubscript{29}(SR)\textsubscript{19}, Au\textsubscript{30}(SR)\textsubscript{20} and Au\textsubscript{31}(SR)\textsubscript{21}) were viewed as stable clusters from mass spectra. Although the structures of these 10e compounds have not yet been given, we expect that the electronic shells of these 10e compounds are analogues of N\textsubscript{2} molecules based on the SVB model.

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Notes and references