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Ligand-Stabilized Gold Clusters

$[Au_{14}(PPh_3)_8(NO_3)_4]$: An Example of a New Class of $Au(NO_3)$-Ligated Superatom Complexes**

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Ultrasmall gold nanoparticles (usNPs) have been of considerable interest because of their unique properties, which arise from size quantization effects[1,2] and thus make them attractive for applications in different areas of nanoscience and nanotechnology.[3,4]

Among usNPs of defined composition, and especially for gold clusters, an outstanding so-called "magic" stability has been observed for certain compositions. This stability has been explained through their specific geometric or electronic structure. In the full-shell cluster model, an usNP is considered as a cut-out of the bulk fcc structure.[5,6] Accordingly, a central metal atom is surrounded by shells of closely packed metal atoms, each shell having $(10n^2+2)$ atoms, n indicating the number of shells. Clusters possessing fully occupied shells consist of 13, 55, 147, … atoms and are supposed to show high stability for geometric reasons, such as the well-studied Schmid cluster $[Au_{55}(PPh_3)_{12}C_{16}]$.[7]

In another model, which goes back to the counting rules introduced by Mingos,[8] metal clusters are considered as superatom complexes formulated as $[L_S{\cdot}A_NX_M]^z$ with electron-withdrawing ligands X or weak Lewis base ligands L attached to the core with metal atoms A and an overall core charge z.[9,10] Accordingly, for Au the 6s electrons are counted and corrected by the number of electrons that are located at electron-withdrawing ligands and corrected by the charge of the cluster. The remaining 6s electrons are placed within the binding delocalized orbitals of the cluster, which is analogous to valence electrons of the atomic theory. Exceptional stability is associated with a total number of:

$$n^* = 2, 6, 12, 20, 30, \ldots \quad (1)$$

electrons for ellipsoidal (2D),[11] and:

$$n^* = 2, 8, 18, 34, 58, \ldots \quad (2)$$

electrons for spherical (3D) quantum dots, corresponding to electron shell closures in an anharmonic mean-field potential. The requirement for a shell-closing electron number therefore follows:

$$n^* = N\,\nu_A - M - z \quad (3)$$

that also takes the atomic valence ν_A (1 for Au) into account. The consideration of clusters as superatom complexes helps to explain the stability of certain gold clusters and conclusively combined the fields of phosphane- and thiolate-stabilized usNPs.

One of the best-known methods to prepare various usNPs consisting of ≤ 13 Au atoms is the reduction of gold salts or complexes with $NaBH_4$.[12] Among these, well-formed dark green crystals of $[Au_9(PPh_3)_8](NO_3)_3$ (**1**) can be obtained reliably by reducing $[Au(PPh_3)NO_3]$ (**2**) in ethanol, followed by further purification and crystallization from diluted solutions.[13] Refined to the space group *Ccca*, the cluster has crystallographic D_2 symmetry with approximate molecular D_{2h} skeletal symmetry derived from a centered icosahedron,[14] and it represents a cluster with closed electronic shell.

Until now, gold clusters that apparently do not fulfill the criteria of neither geometric nor electronic stability, such as clusters consisting of 14 atoms, have only been observed in vacuo by trapped-ion electron diffraction during magnetron sputtering.[15,16]

Herein, we present the first observation of the crystalline compound $[Au_{14}(PPh_3)_8(NO_3)_4]{\cdot}(MeOH)_6$ (**3**), which is stable under ambient conditions. Its unique structure was determined by X-ray diffraction and is discussed in detail and compared to its counterpart **1**. Compound **3** features 1) two neighboring central gold atoms; 2) one of the closest Au−Au distance in usNPs; and 3) NO_3 ligands. Further, **3** is examined under the criteria posed by the concept for superatom complexes and the results of this survey are backed by density functional theory (DFT) calculations of the charge distribution of the highest-occupied molecular orbitals (HOMOs) and lowest-unoccupied molecular orbitals (LUMOs) of **1** and **3**.

During the examination of a batch of crystals of **1** in mother liquor, which were obtained from a relatively concentrated reaction mixture and crystallized from a saturated solution, a few light-green crystal platelets were discovered.

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Although they were very fragile, one of these could be prepared for X-ray analysis (details can be found in the Supporting Information; Table S1 presents a list of important bond distances and angles). A plot of the molecular structure of **3** is shown in Figure 1.

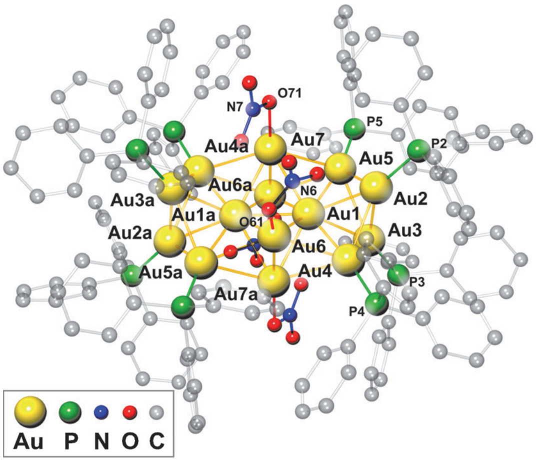

Figure 1. Structure of **3** in the single crystal (hydrogen atoms and solvent molecules omitted for clarity).

The crystal has the space group $P2_1/c$ and the cluster has crystallographic C_i skeletal symmetry, but can also be approximated to D_{2h}. The unit cell contains two Au_{14} cluster molecules and several disordered solvent molecules, of which only six could be refined but not in full detail. As it has been observed for most centered gold clusters, the radial Au–Au bonds (2.6320(4)–2.8248(4) Å) in **3** are generally shorter compared to the peripheral bonds (2.7361(4)–2.9839(4) Å; Supporting Information, Table S1). Furthermore, two new kinds of Au–Au distances are observed in **3**: 1) the distance of the two central Au atoms Au1–Au1a (2.6513(5) Å); and 2) the distance between Au6–Au7a (2.5817(4) Å).

In Table 1, a representative list of Au–Au distances for gold complexes and small clusters ligated by phosphines and thiols and elemental gold is presented. It starts with values of two gold complexes, followed by non-centered clusters up to the number of seven gold atoms per cluster, proceeds with centered clusters, and ends with data for elemental gold. From this table it becomes obvious that Au6–Au7a is the closest proximity observed for gold clusters and phosphine-stabilized gold complexes. Only with regard to $[Au_2(hpp)_2Cl_2]$ (hpp = 2,3,4,6,7,8-hexahydropyrimido[1,2-*a*]pyrimidin-1-ide), where Au^{II} ions are present and the close proximity of Au is forced by the rigidity of the hpp ligand, a shorter distance of 2.47 Å has been found.[17]

Table 1: Au–Au distances for the most common gold complexes, small molecular clusters, and elemental gold. The number of gold atoms increases from the top to the bottom.

Substance	Au–Au distance [Å]	Ref.
$[Au(PPh_3)NO_3]$	3.29[a]	[18]
$[Au_2(dppmH)_2]$	2.883(3)	[19]
$[Au_4(\mu\text{-}I)_2(PPh_3)_4]$	2.649(1)–2.828(1)	[20]
$[Au_5(dppmH)_3dppm]$	2.70-3.01	[21]
$[Au_6(PPh_3)_6](NO_3)_2$	2.651(2)–2.839(2)	[22, 23]
$[Au_7(PPh_3)_7](OH)$	2.58(2)–3.00(2)	[24]
$[Au_8(PPh_3)_7](NO_3)_2$	2.663(5)–2.942(6)	[25]
$[Au_8(PPh_3)_8](PF_6)_2$	2.635(8)–2.960(8)	[26]
$[Au_9(PPh_3)_8](NO_3)_3$	2.6746(9)–2.7079(8)	[13]
$[Au_{11}I_3(P(p\text{-}FC_6H_4)_3)_7]$	2.600(2)–2.942(4)	[27]
$[Au_{11}(Ph_2P(CH_2)_2PPh_2)_6](SbF_6)_3$	2.6294(8)–2.9709(8)	[28]
$[Au_{11}(S\text{-}4\text{-}NC_5H_4)_3(PPh_3)_7]$	2.6295(5)–3.2693(5)	[29]
$[Au_{13}(dppmH)_6](NO_3)_4$	2.773(11)-2.976(11)	[30]
$[Au_{13}(PMe_2Ph)_{10}Cl_2](PF_6)_3$	2.716(2)–2.949(3)	[31]
$[Au_{14}(PPh_3)_8(NO_3)_4]$	2.5817(4)–2.9839(4)	
$[Au_{25}(SCH_2CH_2Ph)_{18}]$	2.773(2)–3.230(2)	[32]
elemental gold	2.884	[33]

[a] Au–Au stacking.

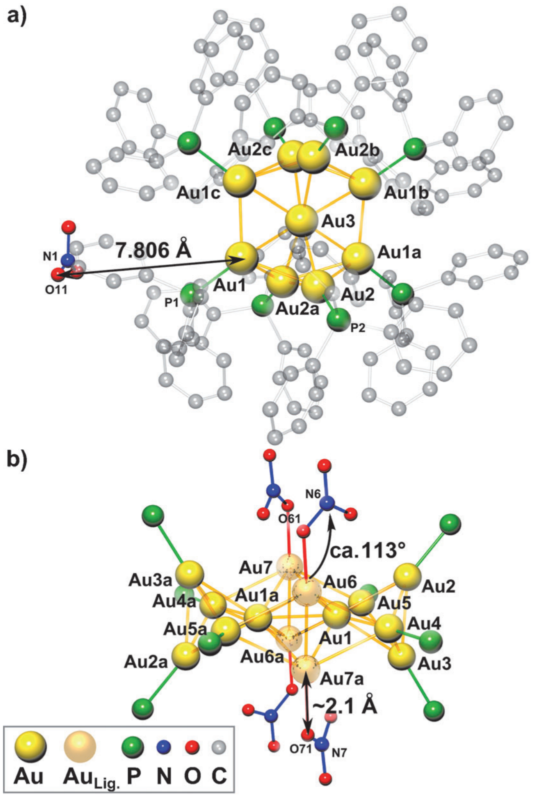

Figure 2. a) Structure of **1** and its closest Au–O distance of 7.806 Å. b) View onto the skeletal structure of **3**, revealing the short Au–O distance of only about 2.1 Å and the Au-O-N angle of about 113°.

Furthermore, **3** is the first gold cluster where $Au(NO_3)$ can be seen to act as a ligand. As an example, in **1** the closest Au–O distance amounts to 7,806 Å, the Au-O-N angle amounts to 99.4°, and one side of the mirror plane σ_h of (NO_3) faces the center of $[Au_9(PPh_3)_8]^{3+}$ (Figure 2a). In contrast, the Au–O distance in **3** is only about 2.1 Å (namely, 2.117(6) Å and 2.126(6) Å), Au-O-N amounts to ca. 113° (113.4(6)° and 111.7(5)°; Supporting Information, Table S1), and σ_h of the NO_3 unit is nearly orthogonal to σ_h of the metal skeleton of **3** (Figure 2b). However, very similar data for the Au–O distance (2.074(8) Å) and Au-O-N angle (115.4(7)°) are present in **2**.[18]

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The skeletal structure of **3** can be derived from **1** by taking the face-fused tetrahedron build up by Au1, Au2, Au3, Au2a, and Au1a, copying it by inversion, and saturating the free coordination sites of the central Au atoms with two pairs of $Au(NO_3)$ moieties (Figure 3).

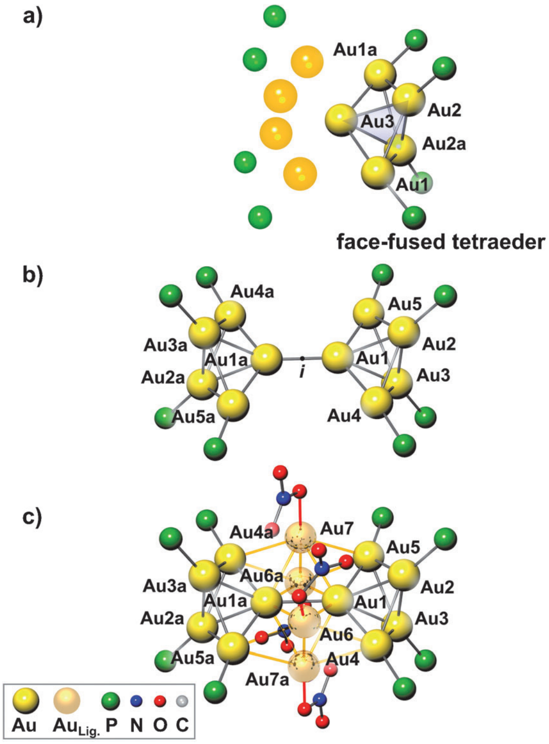

Figure 3. a) Face-fused tetrahedron within the skeletal structure of **1**. The fusion plane is highlighted in blue. b) Transition to the skeletal structure of **3** through copying by inversion and c) saturating the free coordination sites with two pairs of $Au(NO_3)$ moieties.

From the point of view of the superatom complex approach, cluster **1** fulfills the electron count for 2D systems with closed 1s and 2p (binding) states, according to Equations (1) and (3); that is, by applying the formula $[L_8{\cdot}A_9X_0]^{3+}$, the number of shell closing electrons is $n^*=6$. By simple translation of the chemical formula of **3** into $[L_8{\cdot}A_{14}X_4]^0$, $n^*=10$, it neither fulfills n^* for 2D nor for 3D structures. However, respecting 1) the extraordinarily small $(NO_3)Au{-}Au(NO_3)$ distance in **3**; 2) the structural compliance in Au−O distance and Au-O-N angle between **3** and **2**; and 3) the structural relationship between **1** and **3**, it could be assumed that the four $Au(NO_3)$ moieties in **3** should be regarded as electron-withdrawing ligands X. This leads to the corrected formula $[L_8{\cdot}A_{10}X_4]^0$ and $n^*=6$, which is analogous to structure **1** and matches the criteria of an electronically 2D superatom complex.

This formulation is supported by DFT calculations with the B3-LYP functional, which revealed that **3** (Figure 4) as well as **1** (Supporting Information, Figure S1) have an almost two dimensional HOMO and LUMO distribution. An analysis of the charge distribution on the basis of ESP partial charges indicates that each of the $Au(NO_3)$ moieties withdraws approximately 0.5 e from the cluster.

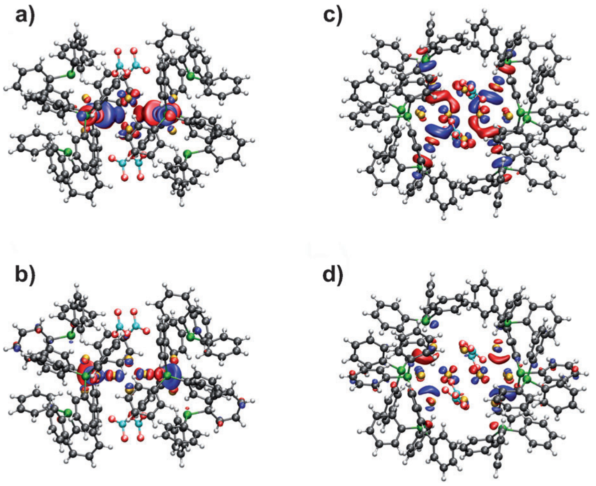

Figure 4. Equipotential surface of the charge distribution of HOMO (a + c)/LUMO(b+d) of **3** from the side of the complex (left panels a + b) and the top (right panels: c + d), color code of the atoms as in Figure 3. A strongly two-dimensional charge distribution on the central cluster is indicated in the HOMO.

To summarize, for the first time a ligand-stabilized cluster with a core consisting of 14 gold atoms, which is stable at ambient conditions, was examined by means of single-crystal X-ray diffraction. Its unique structure bears 1) two neighbored central gold atoms; 2) the closest Au−Au distance observed for gold clusters (2.5817(4) Å); and 3) NO_3 ligands at a Au−O distance of only about 2.1 Å and a Au-O-N angle of about 113°, which is structurally compliant with **2**. The skeletal structure of **3** can easily be generated by combining two face-fused tetrahedron building blocks extracted from **1** followed by the saturation of free coordination sites with two pairs of $Au(NO_3)$ moieties. Finally, verified by DFT calculations, these unique structural features result in an assumed new class of superatom complex stabilized by electron-withdrawing $Au(NO_3)$ units, which will hopefully further support the understanding of certain guiding principles for the molecularly precise synthesis and functionalization of usNPs. Efforts are ongoing to increase the yield of this new cluster for further physicochemical characterization.

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