

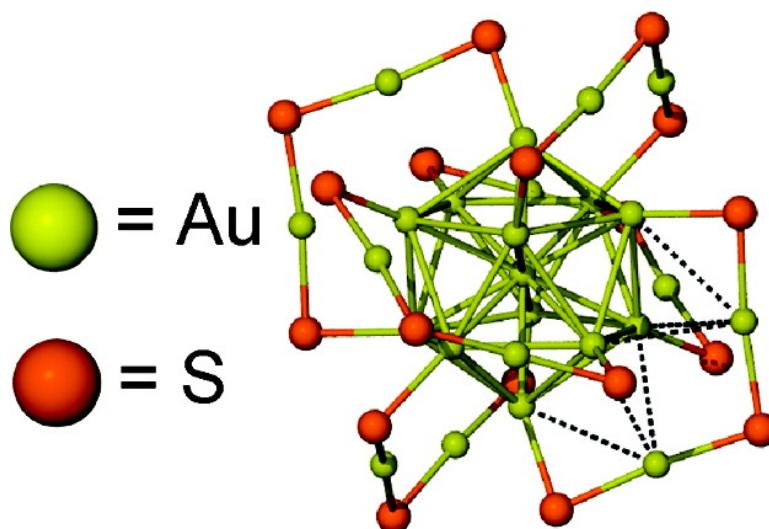
Communication

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Michael W. Heaven, Amala Dass, Peter S. White, Kennedy M. Holt, and Royce W. Murray

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## Crystal Structure of the Gold Nanoparticle $[\text{N}(\text{C}_8\text{H}_{17})_4][\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]$

Michael W. Heaven, Amala Dass, Peter S. White, Kennedy M. Holt, and Royce W. Murray\*

*Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290*

Received January 29, 2008; E-mail: rwm@email.unc.edu

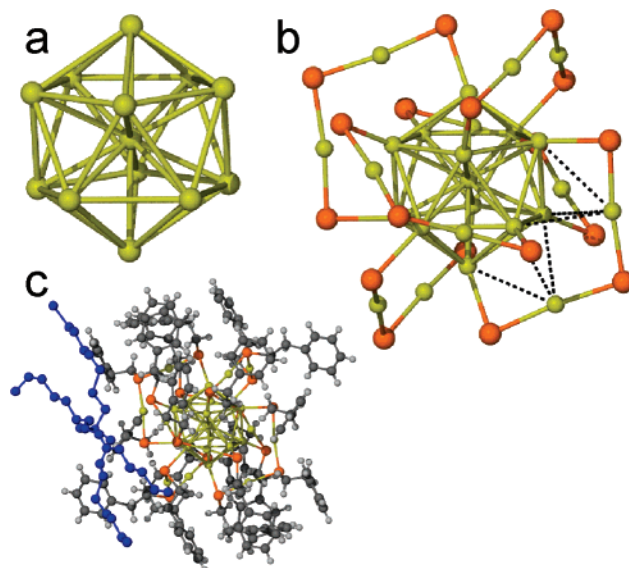
Nanoparticles experience increasing research interest regarding their fundamental properties and industrial applications.<sup>1,2</sup> The former includes particular attention to gold nanoparticles with properties intermediate between molecular and bulk.<sup>2</sup> Nanoparticles with 25 gold atoms ( $\text{Au}_{25}$ ) have been intensively studied.<sup>2a,c,3</sup> Understanding the properties of this (and other) gold nanoparticles has been hindered by a lack of detailed information about how the gold atoms are actually arranged, suggestive research giving various  $\text{Au}_{25}$  conformations including extended interlocked rings<sup>4</sup> or interlinked-platonic solids.<sup>5</sup> Important steps forward were recently taken with the reported<sup>6</sup> crystal structure of  $\text{Au}_{102}(p\text{-SPhCOOH})_{44}$ .

We report here the crystal structure of the thiolate protected gold nanoparticle  $[\text{TOA}^+][\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-$ , where  $\text{TOA}^+ = \text{N}(\text{C}_8\text{H}_{17})_4^+$ . The crystals were synthesized following Whetten's modification<sup>2b</sup> of the Brust reaction<sup>7</sup> (see Supporting Information). The crystal structure revealed an ionic system with triclinic space group  $P\bar{1}$  and a unit cell containing  $[\text{TOA}^+][\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-$  with  $Z = 1$ , as shown in Figure 1 (Figure S-1). The crystal structure reveals three types of gold atoms: (a) one central gold atom whose coordination number is 12 (12 bonds to gold atoms, Figure 1a); (b) 12 gold atoms that form the vertices of an icosahedron around the central atom, whose coordination number is 6 (five bonds to gold atoms and one to a sulfur atom), and (c) 12 gold atoms that are stellated on 12 of the 20 faces of the  $\text{Au}_{13}$  icosahedron. The arrangement of the latter gold atoms may be influenced by auriphilic bonding<sup>8</sup> as exemplified by the dotted bond lines in Figure 1b (also Figure S-2). Together they form six orthogonal semirings of  $(-\text{Au}_2(\text{SCH}_2\text{CH}_2\text{Ph})_3^-)$  around the  $\text{Au}_{13}$  core (Figure 1b).

The positions of the sulfur atoms (orange) of the  $\text{Au}_{25}$  nanoparticle are shown in Figure 1b. Each sulfur atom on the central  $\text{Au}_{13}$  core is connected to two gold atoms. Two sulfur environments are observed in the structure (Figure S-3, S-6): 6 sulfur atoms that are connected to the stellated gold atoms only, with  $\angle_{\text{Au-S-Au}} 101.2 \pm 0.6^\circ$  and 12 sulfur atoms that are connected to one stellated gold atom and to a vertex gold atom on the  $\text{Au}_{13}$  icosahedron, with  $\angle_{\text{Au-S-Au}} 86.7 \pm 0.8^\circ$  (see Supporting Information).

Figure 1c depicts the crystal structure of the entire nanoparticle revealing the interplay between the core anion and  $\text{TOA}^+$  cation. While other stable core charge states have been reported,<sup>9,10</sup> the presence of the  $\text{TOA}^+$  cation confirms the  $1^-$  charge of the native  $\text{Au}_{25}$  nanoparticle, initially revealed in its mass spectrometry.<sup>2a</sup> The nanoparticle has a  $1^-$  core charge state given the reducing environment of its synthesis and the tendency toward two electron occupancy of its low-lying HOMO molecular orbital, revealed in its voltammetry.<sup>10</sup> Thus it is reasonable to assume that Figure 1 reveals the initially formed  $\text{Au}_{25}$  nanoparticle, as opposed to one assembled from smaller nanoparticles.<sup>5</sup>

The thiolate ligand attachment sites are symmetrically distributed on the surface to ensure complete passivation of the nanoparticle. However, the ethylphenyl substituents are oriented to accommodate the  $\text{TOA}^+$  counterion, creating an apparent disorder in the ligand



**Figure 1.** Breakdown of X-ray crystal structure of  $[\text{TOA}^+][\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-$  as seen from [001]. (a) Arrangement of the  $\text{Au}_{13}$  core with 12 atoms on the vertices of an icosahedron and one in the center. (b) Depiction of gold and sulfur atoms, showing six orthogonal  $-\text{Au}_2(\text{SCH}_2\text{CH}_2\text{Ph})_3^-$  “staples” surrounding the  $\text{Au}_{13}$  core (two examples of possible auriphilic bonding shown as dashed lines). (c)  $[\text{TOA}^+][\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-$  structure with the ligands and  $\text{TOA}^+$  cation (depicted in blue) (Legend: Gold = yellow; Sulfur = orange; Carbon = gray; Hydrogen = off-white; the  $\text{TOA}^+$  counterion is over two positions with one removed for clarity).

coverage. At closest approach, the nitrogen cation is situated in a bowl-shaped cleft of the  $\text{Au}_{25}$  nanoparticle surface made up of three of the stellated gold atoms and a triangle of  $\text{Au}_{13}$  core atoms, with an average ionic distance of  $\sim 5.9 \text{ \AA}$  between the nitrogen and  $\text{Au}_{13}$  core edge. The overall diameter of the gold core as measured by the outermost gold atoms is  $9.82 \pm 0.04 \text{ \AA}$  or  $13.01 \text{ \AA}$  using gold van der Waals radii (Table S-1). Taken from the outermost carbon atoms, the overall nanoparticle diameter (in the solid state) is  $23.9 \text{ \AA}$  at its widest. The solid state asymmetry caused by the splaying out of the thiolate ligands by the  $\text{TOA}^+$  implies that, in solution, the overall nanoparticle diameter may be smaller.

The Au–Au distance from the central gold atom to the shell of gold surrounding it in the icosahedral core is  $2.79 \pm 0.01 \text{ \AA}$ , while other Au–Au distances of the core are  $2.93 \pm 0.06 \text{ \AA}$ . The Au–S distance between the icosahedral core gold atoms bonded to sulfur atoms is  $2.38 \pm 0.01 \text{ \AA}$ , while the distance between stellated gold and sulfur atoms is  $2.32 \pm 0.01 \text{ \AA}$  (Figure S-4). These bond lengths are generally typical for Au–Au atom bonding, although there is variation in one case. The Au–Au distances of the pair of core atoms directly below the  $\text{Au}_2(\text{SCH}_2\text{CH}_2\text{Ph})_3$  semirings are slightly squeezed (avg.  $2.81 \text{ \AA}$ ) relative to other core Au–Au bonds (avg  $2.96 \text{ \AA}$ ). This slight distortion of icosahedral cluster symmetry may be due to favorable energetics of the arrangement and formation of the semiring “staples” on the  $\text{Au}_{13}$  core or may be a response to

electrostatic effects caused by the TOA<sup>+</sup> counterion. The Au<sub>13</sub> icosahedral core of Au<sub>25</sub> has important analogies among icosahedral mixed metal and ligand clusters.<sup>11</sup>

The ionic interactions between the Au<sub>25</sub> nanoparticle and the TOA<sup>+</sup> cation produce two zones within adjacent unit cells (Figure S-5). In one direction (along the [100] line), alternating cation–anion interactions produce lipophobic areas, that are surrounded by a sheath of lipophilic ethylphenyl thiolate substituents, clumping together in four distinct bundles. Of course these zones are not isolated but, through extensive  $\pi$ –cation bonding with adjacent nanoparticles in the extended structure, produce a ring of lipophilicity around the ionic portion of the molecular system that likely is revealed in the macro structure by the isolated crystals being long needles.<sup>12</sup>

Intramolecularly and due to symmetry, the ligand shell is divided into two groups, of four and five lipophilic ethylphenyl groups (Figure S-6). The group of four ligands consists of a central phenyl group which acts as an anchor to the other three ligands and provides both the  $\pi$  cloud in one case and the proton for the cation bonding for the other two ligands. The group of five ligands is almost identical except that the fifth ligand interacts with the proton of one of the external phenyl groups, not the central phenyl of the group.

While the icosahedral core as a stable entity in gold clusters had been predicted<sup>13</sup> and seen<sup>5</sup> earlier, the structure here has important relations to the recently reported, much larger Au<sub>102</sub> cluster.<sup>6</sup> In both cases, a core of Au structure is protected by gold thiolate “staples”, but whereas the Au<sub>102</sub> cluster has square Au<sub>3</sub>(*p*-SPh-COOH)<sub>2</sub> gold thiolate staples (with  $\angle_{S-Au-S} \sim 180^\circ$ ) containing rigid *p*-mercaptobenzoic acid thiolates, the semirings that protect (or coat) our Au<sub>13</sub> core are less rigid Au<sub>4</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>3</sub> moieties (with  $\angle_{S-Au-S} = 172.8^\circ$ ) (taking the aurophilic interactions as weaker, see Figure S-2). Like the core, this gold thiolate substructure seems to be a common motif of gold cluster chemistry.<sup>6b</sup>

The present results, contrasting to the earlier<sup>5</sup> Au<sub>25</sub> structure, emphasize the importance of the kinds of ligands in Au nanoparticle structures. The results also regrettably refute previous theoretical predictions;<sup>4</sup> while computational results positioned Au atoms in an icosahedrally equivalent arrangement, the bonding interpretation, supported by experimental Mössbauer spectroscopy, posited several interlocking rings. Crystallographically the present and previous<sup>6</sup> gold-thiolate protected nanoparticle crystal structures appear to form *via* a previously computed “divide and protect” concept.<sup>14</sup> The present crystallographic result may provide a good basis for further theoretical studies.

Au<sub>25</sub> nanoparticles bearing a variety of ligands, including 2-phenylethanethiol,<sup>2</sup> hexanethiol,<sup>8</sup> and glutathione,<sup>2c</sup> have been reported. The stability of the Au<sub>25</sub> nanoparticle and the convergence of other Au atom counts to Au<sub>25</sub> during etching have been stressed recently.<sup>15</sup> Our own research in mass spectrometric analysis<sup>2</sup> of nanoparticles from the Brust and related syntheses also reveals that by far the major product is a Au<sub>25</sub> entity. In light of the crystallographic results, what further can be said about the reason for its stability?

An important point is that the nanoparticle is not a thiolate-protected Au<sub>25</sub> core but a “staple-protected” Au<sub>13</sub> core. This kind of protecting layer may possibly be widespread in gold nanoparticles, and a more complete understanding of “staple” chemistry

becomes an issue. Second, only 12 faces of the icosahedron become Au–S thiolate-bonded. If all were stellated, maximum coverage would produce a Au<sub>33</sub> nanoparticle, which is not seen. The stability rules under which the “staple” motif forms would seem to be crucial to understanding the eventual overall Au atom counts in nanoparticles. These small building blocks may be an important driving force for forming nanoparticles of a particular size during Au nanoparticle synthesis, acting as “monolayer protecting (poly)-ligands” as opposed to single protecting thiolate ligands.

In summary, by revealing the crystal structure of the gold nanoparticle [TOA<sup>+</sup>][Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub>]<sup>–</sup>, the door has been opened to further interpretation of past and future analysis of the common one-pot procedure for production of gold nanoparticles that are links between molecular and bulk gold.

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**Supporting Information Available:** Au nanoparticle synthesis and detailed structural information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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