High-yield synthesis and crystal structure of a green Au\textsubscript{30} cluster co-capped by thiolate and sulfide\textsuperscript{†}

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A green gold-cluster, Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18}, was successfully prepared in high yield and crystallographically characterized. Each cluster consists of an Au\textsubscript{22} core capped by a mixed layer of staple Au-thiolate units, bridging thiolates and a $\mu_3$-S\textsuperscript{2−}.

Since the crystallographic structure determination of Au\textsubscript{102}(p-MBA)\textsubscript{44} in 2007,\textsuperscript{1} thiolate-stabilized metal nanoclusters have attracted increasing research attention owing to their well-defined molecular structures.\textsuperscript{2−7} A series of atomically precise thiolated/selenolated Au nanoclusters have been synthesized and crystallographically characterized.\textsuperscript{8−13} In reported thiolated Au nanoclusters, staple Au\textsubscript{3} units are commonly observed in their surface protected layers. Numerous subsequent studies have demonstrated the influence of both the metal species in the core and capping ligands on the surface features of thiolated metal nanoclusters. No staple units were revealed on the surfaces of thiolated metal nanoclusters where metals other than Au were introduced.\textsuperscript{14−16} Non-staple units were then proposed on the surfaces of Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18} with the molecular structure of Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18} determined by X-ray single crystal analysis.\textsuperscript{†} As illustrated in Fig. 1 and Fig. S2 (ESI†), Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18} is formulated as a neutral cluster with a rod-like Au\textsubscript{32} core capped by a mixed layer of thiolate ligands, gold-thiolate complex units and a S\textsuperscript{2−}. The mixed surface capping layer consists of two Au\textsubscript{3}S\textsubscript{2} staple units, two AuS\textsubscript{2} units, six bridging thiolate SR ligands and one S\textsuperscript{2−}. Although the Au-thiolate staple units\textsuperscript{14−16} and bridging thiolates\textsuperscript{18−20} have been previously revealed as important surface capping motifs in the reported structures of thiolated-Au nanoclusters, the presence of surface $\mu_3$-S\textsuperscript{2−} motifs has not been previously observed in thiolated Au nanoclusters.

To incorporate S\textsuperscript{2−} onto the surface of thiolated Au nanoclusters, Na\textsubscript{2}S was introduced deliberately in the synthesis of Au nanoclusters. In a typical synthesis of Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18} nanoclusters (ESI†), HAuCl\textsubscript{4} and tert-butylthiol (t-C\textsubscript{4}H\textsubscript{9}SH) (1:3 molar ratio) were combined in tetrahydrofuran (THF). After stirring for 15 min at 55 °C, aqueous solutions of NaBH\textsubscript{4} and Na\textsubscript{2}S were added simultaneously into the mixture of HAuCl\textsubscript{4} and t-C\textsubscript{4}H\textsubscript{9}SH. The ratio of HAuCl\textsubscript{4}:NaBH\textsubscript{4}:Na\textsubscript{2}S was 50:500:1. The reaction mixture turned dark-brown immediately and was kept under stirring at 55 °C for another hour. After the aqueous layer was removed, toluene and excess t-C\textsubscript{4}H\textsubscript{9}SH were added to the reaction mixture whose temperature was then raised to 60 °C. The solution gradually changed from dark-brown to dark-green in the following 6 h stirring at 60 °C. Brown sheet-like single crystals of Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18} were recrystallized by diffusing hexane into the cluster solution in CH\textsubscript{2}Cl\textsubscript{2} at 4 °C over 15 days. The crystals were readily redissolved in toluene to give a green solution.

The molecular structure of Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18} was determined by X-ray single crystal analysis.\textsuperscript{§} Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18} clusters are crystallized in the triclinic space group $P\bar{1}$ (Fig. S1, ESI†). As illustrated in Fig. 1 and Fig. S2 (ESI†), Au\textsubscript{30}S(S\textsubscript{Bu})\textsubscript{18} is formulated as a neutral cluster with a rod-like Au\textsubscript{32} core capped by a mixed layer of thiolate ligands, gold-thiolate complex units and S\textsuperscript{2−}. The mixed surface capping layer consists of two Au(SR\textsubscript{2}) staple units, two Au(SR\textsubscript{3}) units, six bridging thiolate SR ligands and one S\textsuperscript{2−}. Although the Au-thiolate staple units\textsuperscript{14−16} and bridging thiolates\textsuperscript{18−20} have been previously revealed as important surface capping motifs in the reported structures of thiolated-Au nanoclusters, the presence of surface $\mu_3$-S\textsuperscript{2−} motifs has not been previously observed in thiolated Au nanoclusters.

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While the Au$_{20}$ core in Au$_{30}$(TBBT)$_{20}$ is protected by four Au$_3$(SR)$_3$ staple units and eight bridging SR ligands, no comparable Au$_3$(SR)$_3$ staple units are revealed on the surface of Au$_{30}$S(SrBu)$_{18}$ for which a diversity of surface motifs are identified. As shown in Fig. 1b and Fig. S3 (ESI†), each of the two Au$_3$(SR)$_3$ staple units is capping an end of the Au$_{13}$ core with the terminal thiolates binding to Au atoms on the bicuboctahedral unit. The two Au(SR)$_2$ units bind at the sides of the rod-like Au$_{13}$ core with one thiolate coordinating to an Au atom on the bicuboctahedral unit and the other to a capping Au atom. Similar to the situation in [Au$_3$(SC$_6$H$_4$I)$_3$]$_{16}$, each of the two face-capping Au atoms in the core forms a linker between the Au$_3$(SR)$_3$ and Au(SR)$_2$ units. The Au$_{13}$ core is further bound by four bridging SR at its sides, two bridging SR ligands on both ends, and one $\mu_3$-S$^2$– on one end. The average Au–S bond length/Au–S–Au bond angle are 2.311 Å/96.281° and 2.330 Å/97.337° in the Au$_3$(SR)$_3$ and Au(SR)$_2$ units, respectively. Compared with those in staple units, the average Au–S–Au bond angle (92.22°) at the six bridging SR ligands is smaller and their average Au–S bond length (2.338 Å) is slightly longer.

Only one $\mu_3$-S$^2$– is present on the surface of Au$_{30}$S(SrBu)$_{18}$, rendering the cluster asymmetric due to its location at one end of the Au$_{22}$ core. The $\mu_3$-S$^2$– binds to two adjacent Au atoms on the bicuboctahedral Au$_{30}$ unit and to one Aucap atom as described above. Such a coordination mode differentiates the binding structures of the two face-capping Au atoms in the Au$_{13}$ core. While the Aucap at the end without $\mu_3$-S$^2$– binding caps an Au$_4$ square, the other Aucap only caps three Au atoms of the bicuboctahedral unit. Although observed in small Au clusters, the presence of $\mu_3$-S$^2$– surface motifs has not been well reported in large thiolated Au nanoclusters. The unique $\mu_3$-coordinated sulfide on an Au cluster presents an opportunity to create custom-modified thiolated Au nanoclusters with the potential for targeted functionality and applications.

As illustrated in Fig. 3a, the UV-Vis spectrum of Au$_{30}$S(SrBu)$_{18}$ in toluene displays one major absorption peak at 620 nm and two shoulder peaks around 375 nm and 475 nm (Fig. 3b). Such an optical absorption of Au$_{30}$S(SrBu)$_{18}$ is very similar to that of the all-thiolate-protected Au$_{30}$(SrBu)$_{18}$ cluster. Very recently, Dass and coworkers also obtained single crystals of Au$_{30}$(SrBu)$_{18}$ during the crystallization of chromatographically purified Au$_{30}$(SrBu)$_{18}$. With the use of a trace amount of Na$_3$S, we demonstrate a high-yield, high-purity synthesis of Au$_{30}$S(SrBu)$_{18}$ in a one-pot method.

As depicted in Fig. 2, the Au$_{22}$ core of Au$_{30}$S(SrBu)$_{18}$ can be better described structurally as a rod-like Au$_{13}$ unit face-capped by two Au atoms. Au$_{20}$ is a bicuboctahedral unit consisting of two distorted interpenetrating Au$_{13}$ cuboctahedrons, similar to the Au$_{20}$ core of Au$_{28}$(TBBT)$_{20}$ [10]. In the core of Au$_{30}$S(SrBu)$_{18}$, however, the Au$_{20}$ unit is further face-capped by two Au atoms at either end, resulting in the formation of a rod-like Au$_{13}$ core. The average Au–Au bond length of the Au$_{13}$ bicuboctahedron is 2.89 Å which is comparable to the bond length in bulk gold (2.88 Å) and shorter than the bond length of the Au$_{20}$ kernel of Au$_{28}$ (2.92 Å).

The presence of two additional face-capping Au atoms (Aucap) in the core of Au$_{30}$S(SrBu)$_{18}$ significantly modifies the surface binding structure when compared with that of Au$_{28}$(TBBT)$_{20}$.
without purification. The crude reaction product of this synthesis displayed an identical UV-Vis absorption to that of single crystals of Au$_{30}$S(SBu)$_{18}$ dissolved in CH$_2$Cl$_2$ (Fig. 3a). To confirm the high purity of Au$_{30}$S(SBu)$_{18}$ in the reaction mixture, the mass spectra of both the crude product and the pure crystals were further analysed. A clean and strong peak with m/z of 7457 is clearly observed in both mass spectra (Fig. 3c and Fig. S4, ESI†). The peak is assigned to [Au$_{30}$S(SBu)$_{17}$]$^+$ which corresponds to the loss of one SBu$^-$ group from the Au$_{30}$S(SBu)$_{18}$ cluster. These results demonstrate the high purity of Au$_{30}$S(SBu)$_{18}$ in the crude product. When the laser intensity used in the MALDI-MS measurements was increased, further loss of organic ligands from the cluster was observed (Fig. S5, ESI†). The high-yield production of Au$_{30}$S(SBu)$_{18}$ on introducing Na$_2$S could be rationalized by the presence of $\mu_3$S$^2$– which helps to relieve the steric pressure caused by the adjacent five SBu groups. It should be noted that Au$_{30}$S(SBu)$_{18}$ is not luminescent while strongly absorbing in the UV-Vis region.

In conclusion, a new gold-nanocluster, Au$_{30}$S(SBu)$_{18}$, was successfully synthesized and structurally determined by single crystal analysis. The introduction of a trace amount of Na$_2$S was found to be critical for achieving the high-yield synthesis of Au$_{30}$S(SBu)$_{18}$. While the core of Au$_{30}$S(SBu)$_{18}$ is an Au$_{22}$ unit that can be described as a bicuboctahedral Au$_{20}$ unit capped by two Au atoms, the surface layer of the cluster consists of two Au$_3$(SR) staple units, two Au(SR)$_2$ units, six bridging SR ligands and one $\mu_3$S$^2$–. The presence of $\mu_3$S$^2$– on a thiolated Au nanocluster provides opportunities to create and manipulate surface structures of thiolated Au nanoparticles.

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**Notes and references**

The diffraction patterns measured for the compound are dominated by the scattering from the Au$_{30}$S$_3$ core with almost 3000 electrons whereas the less ordered tertiary butyl shell contains fewer than 600 electrons distributed in a considerably large volume. The structure analysis is complicated by the occurrence of twinning which appears to be an inherent property of crystals of this material. Review of the diffraction images confirmed this diagnosis and calculated precession layers demonstrated that additional smaller twin components may also be present. Residual electron density in the core region is ascribed to minor twin components which were not modeled. A large void in the structure, ~22% of the cell volume, has a calculated electronic content of ~400 and is consistent with occupation by disordered solvent. A detailed description of the structure analysis is provided in the CIF.