

Ligand-Protected Gold Clusters – Synthesis, Structures, and Stabilities

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Free gold clusters have been prototypical systems for the study of structures, stabilities and physicochemical properties of metal clusters. For fabrication of cluster-based materials with desired properties, it is essential to understand the effect of protecting ligands on the structures and stabilities of gold clusters. We have developed an experimental method to synthesize a family of ligand-protected gold clusters with well-defined compositions. Crucial step for our precision synthesis is to fractionate as-prepared, polydisperse gold clusters by size using polyacrylamide gel electrophoresis, size exclusion chromatography, or solvent extraction. Charge states and molecular formulas of the fractionated clusters were determined by electrospray-ionization mass spectrometry. In the present contribution, we discuss the structures and stabilities of the gold clusters protected by phosphines and thiolates.

Bidentate phosphine ligand:

It is known that gold clusters protected by monodentate phosphines such as $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ are not so stable because of weak Au-PR_3 interaction [1]. By using a bidentate phosphine ligand, BINAP, we obtained a stable compound $[\text{Au}_{11}(\text{BINAP})_4\text{Cl}_2]^+$ [2]. The formal charge of the Au_{11} core is 3+, so that the preferential formation is due to high stability associated with electronic shell closing.

Thiolate ligands:

Because of a strong Au-SR bonding, as-prepared samples of $\text{Au}_n(\text{SR})_m$ usually contained metastable clusters kinetically stabilized in addition to thermodynamically stable clusters [3-5]. By depopulating these metastable clusters by chemical etching, we could isolate $\text{Au}_{25}(\text{SR})_{18}$ [6-9], $\text{Au}_{38}(\text{SR})_{24}$ [5,10], $\text{Au}_{144}(\text{SR})_{59}$ [10] as stable compounds. Charge states of these clusters were not fixed but could be altered in the range of -1 to +3 dependent on the conditions of preparation and storage [9,10]. Moreover, these $\text{Au}_n(\text{SR})_m$ clusters show reversible redox behavior in contrast to $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$. These results suggest that geometrical factors play more important role in determining the stability of $\text{Au}_n(\text{SR})_m$. Possible geometric structures are proposed for $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{144}(\text{SR})_{59}$ in which highly-symmetrical Au cores are fully protected by [-SR-Au-SR-] and/or [-SR-Au-SR-Au-SR-] oligomers, based on the structures of the relevant systems $[\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^-$ [11-13] and $\text{Au}_{102}(\text{SC}_6\text{H}_4\text{COOH})_{44}$ [14].

Mixed ligands: [15]

Chemical reaction between $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$ and C_nSH ($n=2-18$) serendipitously yielded a stable compound $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_n)_5\text{Cl}_2]^{2+}$. Single crystal XRD analysis revealed that Au_{25} core forms a cluster-of-cluster structure; two icosahedral Au_{13} cores are bridged by thiolates sharing a vertex atom (see Figure).

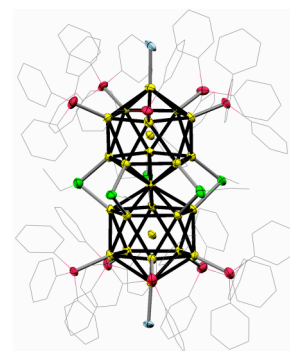


Figure. Ortep drawing of $[\text{Au}_{25}(\text{SC}_2)_5(\text{PPh}_3)_{10}\text{Cl}_2]^{2+}$

[1] Schmid, G. *et al.*, *Chem. Ber.* **1981**, *114*, 3634. [2] *J. Phys Chem. B* **2006**, *110*, 11611. [3] *J. Am. Chem. Soc.* **2006**, *128*, 6036. [4] *J. Phys. Chem. B* **2006**, *110*, 12218. [5] *J. Phys Chem. C* **2007**, *111*, 4153. [6] *J. Am. Chem. Soc.* **2005**, *127*, 5261. [7] *J. Am. Chem. Soc.* **2005**, *127*, 13464. [8] *Small* **2007**, *3*, 835. [9] *J. Am. Chem. Soc.* **2007**, *129*, 11322. [10] *J. Am. Chem. Soc.* in press. [11] Heaven, M. W. *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 3754. [12] Akola, J. *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 3756. [13] Zhu, M. *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 5883. [14] Jadzinsky, P. D. *et al.*, *Science* **2007**, *318*, 430. [15] *J. Phys Chem. C* **2007**, *111*, 7845.