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Au_{20} Nanocluster Protected by Hemilabile Phosphines

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Supporting Information

ABSTRACT: A novel phosphine-protected Au_{20} nanocluster was isolated through the reduction of $Au(PPhpy_2)Cl$ by $NaBH_4$ ($PPhpy_2$ = bis(2-pyridyl)-phenylphosphine). Its composition was determined to be $[Au_{20}(PPhpy_2)_{10}Cl_4]Cl_2$, and single crystal X-ray structural analysis revealed that the Au_{20} core can be viewed as being generated from the fusion of two Au_{11} clusters via sharing two vertices. Optical absorption spectroscopy indicated this Au_{20} has a large HOMO−LUMO gap ($E_g \approx 2.24$ eV). This is the first example of a ligand-protected gold nanocluster with a core generated from incomplete icosahedral Au_{11} building units.

Gold-nanoclusters receive an intense interest due to their relevance to a variety of properties including luminescence, catalysis, and biological applications.[1] Ligand-protected gold nanoclusters having well-defined compositions and structures are of great significance in terms of the correlation of structures and properties. So far, a large number of ligand-protected gold clusters have been prepared, and mass spectrometry has been the main technique to identify their compositions.[2] Unambiguous determination of the structures of the clusters is a challenge due to the difficulties in obtaining X-ray quality single crystals. In this regard, significant advances have been made with thiolate-protected gold nanoclusters. The crystal structures of Au_{102},[3] Au_{25},[4] and Au_{38}[5] have been determined. Regarding phosphine-protected gold nanoclusters, the structures of small ones such as Au_{4-10}, Au_{11} and Au_{13} are known,[6] and their formation mechanism and electronic structures have attracted recent attention.[7,8] However, there is only one structurally characterized phsophine-protected gold nanocluster beyond Au_{13}, $[Au_{39}(PPh_3)_{14}Cl_6]Cl_2$.[9]

Icosahedral Au_{13} motif is an important basic unit for most known structures with nuclearity higher than 13. Au_{25} was found having a structure with a Au_{13} core with RS-Au-SR-Au-SR staples attached.[4,10] Homonuclear structures such as a vertex-sharing biicosahedra in $[Au_{25}(PPh_3)_{10}(SC_2H_5)_5Cl_2]^{2+}$,[11] a face fusing biicosahedral Au_{23} in $Au_{38}(SR)_{24}$ have been reported.[5] Cyclic triicosahedra[12a] and interpenetrated biicosahedra[12b] have been founded in Au−Ag mixed metal clusters. Herein, we report a structurally determined Au_{20} cluster with a unique core structure, which can be viewed as the fusion of two incomplete icosahedral Au_{11} units.

Both phosphines and thiolates have been used in the preparation of ligand-protected gold nanoclusters. Au−P bonds are weaker than Au−S bonds. Normally, a phosphine is neutral but a thiolate possesses a negative charge; phosphines are terminal ligands, while thiolates can bridge gold centers. In an attempt to increase the stability of phosphine-protected gold nanoclusters, our synthetic strategy is the use of pyridyl phosphines. A pyridyl phosphine contains P and N donors, which makes it available for bridging two metal centers as well as protecting gold atoms.

Typicallly, to 3.5 mL of ethanol suspension containing 0.20 mmol $Au(PPhpy_2)Cl$, a freshly prepared solution of $NaBH_4$ (0.05 mmol in 1 mL of ethanol) was added dropwise under vigorous stirring. The color was immediately changed from white to orange and to black. The reaction continued for 24 h at room temperature in air under the exclusion of light. A small amount of brown solid appeared at the flask bottom. Twenty milliliters of *n*-hexane was added to give a brown precipitate, which was collected by filtration. This crude solid was dissolved in a mixture of solvents containing 3 mL of CH_2Cl_2 and 0.2 mL of methanol, and the resulting solution was subject to diffusion of ether to afford black crystals after ca. 10 days (7.2 mg yield 10.1% based on Au). The identity was determined to be $[Au_{20}(PPhpy_2)_{10}Cl_4]Cl_2$ (**1**). ^{31}P NMR shows one singlet at 52.2 ppm, which indicates the phosphines have fast dynamic behavior in solution. TGA indicated that the loss of the cocrystallized solvent molecules happened below 130 °C.

Single crystal structural analysis revealed that **1** crystallizes in triclinic with $P\bar{1}$ space group.[13] It comprises a dicationic cluster $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$ and two chloride counteranions. The structure of the centrosymmetric cation is shown in Figure 1, which consists of a Au_{20} core, 10 phosphines and four chloride ligands. The Au···Au distances from the interstitial atom to the surface ones are in the range of 2.6438(9)−2.815(1) Å except for a longer one being 2.992(1) Å, and the separation between two interstitial gold atoms is 3.141(1) Å. The waist of the core is clutched by four PN bridges, and the P and N donors of the phosphines are bound to two Au atoms (Figure 2a). Four chlorides are additionally coordinated to the cluster core with Au−Cl bond lengths being 2.365(5) and 2.375(6) Å.

The Au_{20} skeleton could be viewed as the fusion of two Au_{11} incomplete icosahedra. As illustrated in Figure 2b, two Au_{11} clusters join together via the sharing of the green vertices to generate the Au_{20} core structure, which results in the formation of five additional gold−gold bonds including four on edge and one connecting two interstitial gold atoms.

The sample was further characterized by a high-resolution Fourier transform ICR spectrometer with an electrospray ionization source in positive mode (Figrue 3a). Although $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$ was not found, intense peaks at m/z =

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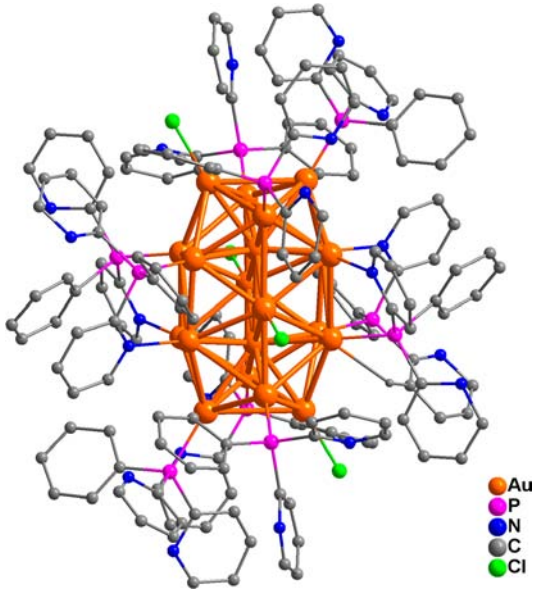

Figure 1. The structure of the dicationic $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$ cluster in **1**.

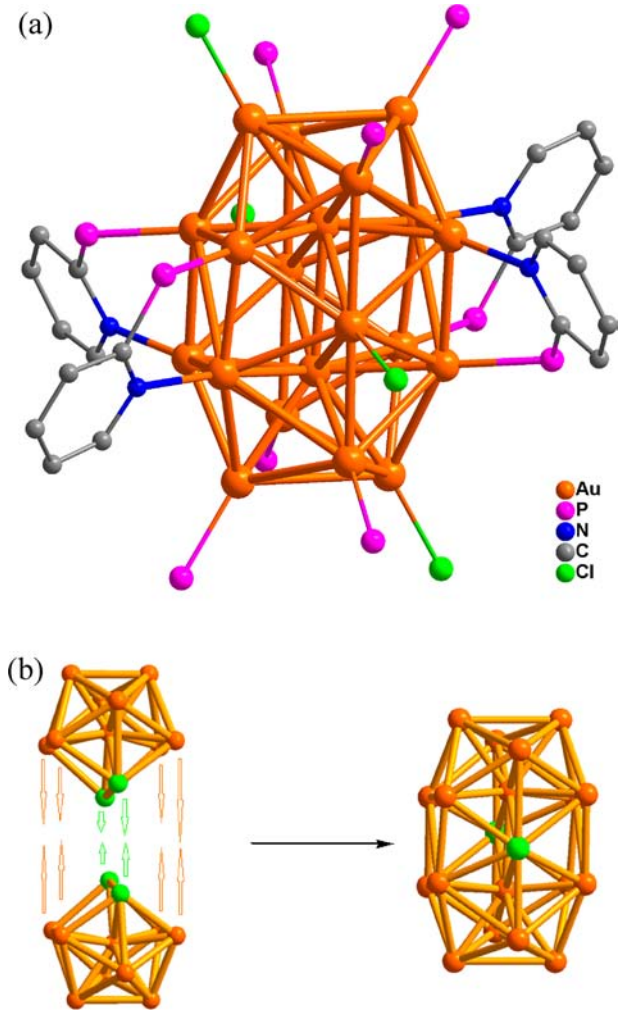

Figure 2. (a) The bridging mode of $PPhpy_2$ in **1**; phenyl and pyridyl groups not linked to Au atoms have been omitted for clarity. (b) Anatomy of the Au_{20} core structure in **1**, two green atoms denote the shared vertices.

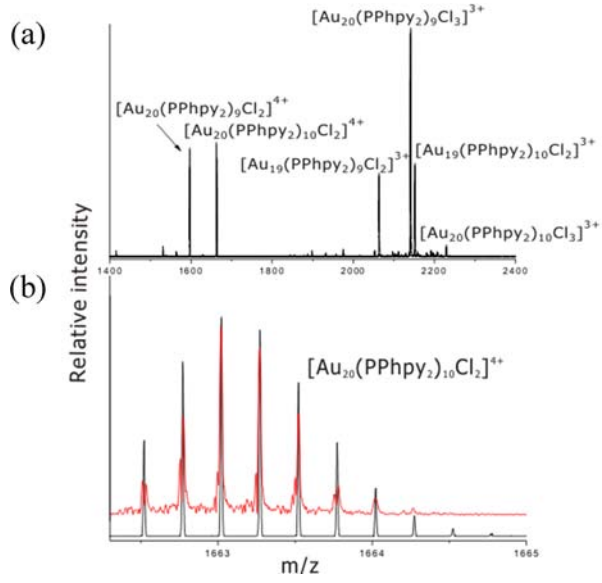

Figure 3. (a) Mass spectrum of the Au_{20} cluster. (b) The measured (red trace) and simulated (black trace) isotopic patterns of $[Au_{20}(PPhpy_2)_{10}Cl_2]^{4+}$.

1662.985 was observed, which corresponds to $[Au_{20}(PPhpy_2)_{10}Cl_2]^{4+}$ derived from the removal of two chlorides from $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$. The observed isotopic pattern of $[Au_{20}(PPhpy_2)_{10}Cl_2]^{4+}$ is perfectly in agreement with the simulated one (Figure 3b). Another prominent species observed at m/z = 2141.248 corresponds to $[Au_{20}(PPhpy_2)_9Cl_3]^{3+}$. This observation indicates that chloride and phosphine ligands can be readily dissociated from **1**.

This Au_{20} cluster is quite stable. It is confirmed by UV−vis spectra that no decomposition was observed after its solution had been stored under ambient conditions for a week. The fragmentation pattern in Figure 3 also shows that the Au_{20} skeleton can be retained under the ionization conditions with the leave of chloride or phosphine ligands.

The total number of valence electrons of $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$ is calculated to be 14 (n = 20 − 4 − 2). It does not match a case of shell closure, which suggests that Au_{20} is stabilized by geometrical factors. The bridging of PN donors of hemilabile phosphines makes large contribution to the stabilization of the nanocluster.

It was reported that bare Au_{20} has a tetrahedral (T_d) structure with a HOMO−LUMO energy gap of 1.77 eV.[14] Wang et al. identified the composition of a phosphine-protected Au_{20} to be $Au_{20}(PPh_3)_8^{2+}$ by mass spectrometry, which was computed to have tetrahedral structure.[15] Jin et al. reported a thiolate-protected Au_{20} cluster with a composition of $Au_{20}(SCH_2CH_2Ph)_{16}$, which was also determined by mass spectrometry, and the structure has not been determined.[16] Zen et al. performed a calculation on this Au_{20} cluster, and predicted that it has a prolate Au_8 core and four −RS-Au-RS-Au-RS-Au-RS- extended staple motifs.[17] The present work represents the first structural determination of a Au_{20} cluster.

The UV−vis absorption spectrum of **1** in CH_2Cl_2 shows three prominent absorption bands at 493, 344 (shoulder), and 260 nm. The 260 nm band comes from the intraligand transition of the $PPhpy_2$ ligand, as a similar band is found in a CH_2Cl_2 solution of pure $PPhpy_2$. The optical energy gap was determined to be 2.24 eV (Figure 4 inset), which is much higher than 1.77 eV found in bare Au_{20}. It is noteworthy that

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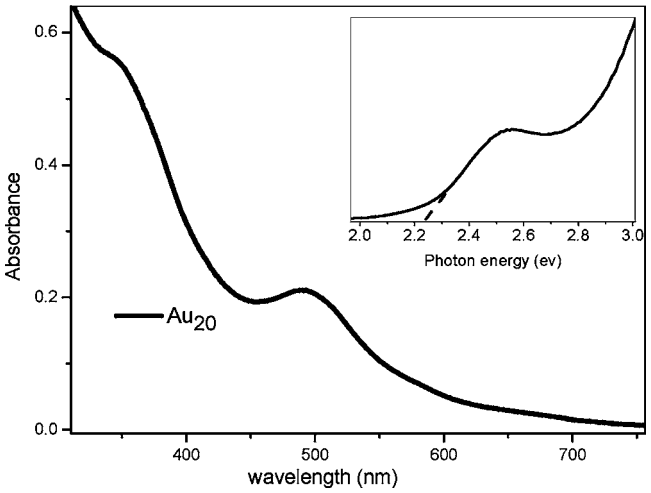

Figure 4. The optical absorption spectrum of **1** in methylene dichloride. (Inset) The spectrum on the energy scale (eV); the HOMO−LUMO gap is 2.24 eV.

the absorption profile of **1** is quite similar to that of $Au_{20}(SCH_2CH_2Ph)_{16}$, and the HOMO−LUMO gap of **1** is just a little higher than that in $Au_{20}(SCH_2CH_2Ph)_{16}$ (2.15 eV).

This work demonstrates that a new cluster core Au_{20} has been obtained with the use of hemilabile phosphines. The bridging ability of hemilabile phosphines enhances the stability of the Au_{20}. The arrangement of the Au_{20} core structure suggests that the incomplete icosahedral motifs may be taken into consideration in making prediction of the structures of gold clusters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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