

Isolation and Tandem Mass Spectrometric Identification of a Stable Monolayer Protected Silver–Palladium Alloy Cluster

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Supporting Information

ABSTRACT: A selenolate-protected Ag–Pd alloy cluster was synthesized using a one-pot solution-phase route. The crude product upon chromatographic analyses under optimized conditions gave three distinct clusters with unique optical features. One of these exhibits a molecular peak centered at m/z 2839, in its negative ion mass spectrum assigned to Ag₅Pd₄(SePh)₁₂⁻, having an exact match with the corresponding calculated spectrum. Tandem mass spectrometry of the molecular ion peak up to MS⁹ was performed. Complex isotope distributions in each of the mass peaks confirmed the alloy composition. We find the Ag₃Pd₃⁻ core to be highly stable. The composition was further supported by scanning electron microscopy, energy-dispersive spectroscopy, and X-ray photoelectron spectroscopy.



SECTION: Physical Processes in Nanomaterials and Nanostructures

N oble metal clusters with monolayer protection are becoming one of the most fascinating areas of contemporary chemical research. They have been used in several applications¹⁻¹² because of their unique optical properties, especially photoluminescence.^{13–16} Among them, gold clusters have been studied extensively. Crystal structures of several gold clusters such as Au_{23} ,¹⁷ Au_{25} ,^{15,18} Au_{28} ,¹⁹ Au_{30} ,²⁰ Au_{36} ,²¹ Au_{38} ,²² and Au_{102} ,²³ have been reported. Silver clusters have been studied to a lesser extent,^{24–26} although reports exist on $Ag_{7,8}$,²⁷ Ag_{9} ,²⁸ Ag_{14} ,²⁹ Ag_{16} ,³⁰ Ag_{32} ,³¹ Ag_{44} ,^{32,33} and Ag_{152} ,⁴⁴ with detailed characterization, dominated by mass spectrometry. Reports of mixed ligand (phosphine and thiol)-protected Ag_{14} ,²⁹ Ag_{16} ,³⁰ and Ag_{32} ,³⁰ are also there. Recently, crystal structure of the very first complete thiol-protected core, namely, Ag_{44} ,^{35,36} has been solved. A limited number of studies exist on other metal clusters like Pt,³⁷ Cu,³⁸ and so on. However, synthesis of atomically precise alloy clusters of various compositions is a challenge, and very few reports exist in the literature;^{39–41} examples include PdAu₂₄,⁴² Pd₂Au₃₆,⁴³ PdAu₁₀,⁴⁴ and Ag_7Au_6 ,⁴⁵ all of which have thiol protection. Selenolate-protected single metal clusters such as Au_{25} ,⁴⁶ Au_{18} ,⁴⁷ Au_{38} ,⁴⁸ Au_{24} ,⁴⁹ and Ag_{44} ,³³ have been reported, whereas only one alloy, namely, Cu_nAu_{25-n} (n = 1-9),⁵⁰ is known with such monolayers. So far, to the best of our knowledge, there is no report on Ag–Pd alloy clusters.

We report the very first selenolate protected Ag–Pd alloy cluster. The crude cluster was synthesized from silver trifluoroacetate(s) and sodium tetracholopalladate(s) in the presence of benzeneselenol (l) (details are in Supporting Information 1). Solid NaBH₄ was added, and stirring was continued. The color change of orange to yellowish brown indicated the conversion of selenolates to clusters (Figure S2 in the Supporting Information). Several analytical methods were used to characterize the clusters (Supporting Information 1).

The crude clusters show the presence of molecule-like features in absorption spectroscopy (Figure 1). The spectrum gives peaks near 400 (3.1), 381 (3.25), 326 (3.8), 282 (4.4), and 248 (4.99) nm (eV) and a small hump at 590 (2.1) nm (eV). The crude cluster was subjected to HPLC for purification using acetonitrile as the solvent in the isocratic mode. Several parameters such as the pump pressure, solvents, flow rate, temperature, and so on were optimized to achieve the isolation process. Slower flow rate leads to longer time for the cluster to come out, but isolation becomes easier as expected (Figure S3 in the Supporting Information). The best separation was observed with 0.25 mL/min flow rate at room temperature. The corresponding chromatogram gives three well-separated peaks (Figure 1) at retention times of 6.44, 7.69, and 10.70 min, which have been marked as clusters 1, 2, and 3, respectively. Characteristic UV/vis features were observed for different isolated species (Figure 1a and Figure S4 in the Supporting Information). Cluster 1 shows peaks at 3.27 (379), 3.94 (315), 4.4 (282), and 4.8 (258) eV (nm) and a small hump at 1.93 eV (642 nm), whereas cluster 2 has peaks at 3.1 (400), 3.8 (326), 4.47 (277), and 4.9 (253) eV (nm) and a small hump at 2.1 (590) eV (nm). Compared with clusters 1 and 2, cluster 3 shows a different nature, and it has multiple humps at 1.9 (653), 2.8 (443), 3.3 (376), 3.8 (326), 4.4 (282)

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Figure 1. HPLC chromatogram of the crude cluster in acetonitrile at room temperature (30 °C) using the isocratic mode. Flow rate was optimized at 0.25 mL/min. The UV/vis detector was used for analysis. Three distinct peaks correspond to clusters 1–3. Inset: (a) UV/vis spectra of as-synthesized (i) crude and (ii) cluster 2; inset of inset shows the corresponding photographs of the cluster solutions (marked as i' and ii', respectively). (b) HRTEM image of cluster 2. (c) Size distribution. A few particles are marked with yellow circles.

eV (nm) and 4.9 (253) eV (nm). Each cluster has its own characteristic color, which makes them distinguishable from each other as well as from the crude cluster (Figure 1a and Figure S4 in the Supporting Information).

Electrospray ionization mass spectrometry (ESI MS) is known to be the best tool for precise characterization of clusters.^{28,51} The assignment can be made based on the molecular ion peak and various charged species of the parent ion. Comparison with the corresponding calculated spectrum can be useful. Observation of good isotopic distribution can also be a strong support for predicting the elements present in the cluster as well as the composition. Here the crude as well as all isolated clusters have been subjected to ESI MS. First, the ESI MS of the crude cluster was analyzed in the negative ion mode with acetonitrile as the solvent. No characteristic peaks were observed in the positive ion mode. Only negative ions were detected. The crude cluster shows a peak centered at m/z2839 (Figure S5A in the Supporting Information) along with some selenolate fragments at lower mass regions. For cluster 1 (Figure S5B in the Supporting Information), many peaks were observed, but isotope distribution was not seen, and they appeared broad. Cluster 3 (Figure S5D in the Supporting Information) does not show significant peaks in both negative and positive modes. For cluster 2, the spectrum shows (Figure 2 and Figure S5C in the Supporting Information) a molecular ion peak at m/z 2839 along with some fragments at m/z 2604 and 2204, which have been assigned as [Ag₅Pd₄(SePh)₁₂]⁻, [Ag₅Pd₄(SePh)₁₀Se]⁻, and [Ag₃Pd₃(SePh)₁₀]⁻, respectively. The fragments are due to (SePh+Ph) and Ag₂Pd(SePh)₂ losses, respectively (Figure 2). The isotope distribution of the molecular ion peak shows an exact match with the corresponding calculated one (Figure 2a). Differences between the spectra are very small and are hardly noticeable. Absence of selenolate fragments in the lower mass region confirms the purity of the isolated cluster (Figure S5 in the Supporting Information). The fragment at m/z 2204 appears with reasonable intensity, which contains the unusual metallic core of Ag₃Pd₃ protected with ligands and the absence of fragments from this species, suggesting its stability.



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Figure 2. ESI MS data of cluster 2. All peaks are assigned to their compositions. Inset: (a) Calculated (red trace) and experimental (black trace) mass spectra of $[Ag_5Pd_4(SePh)_{12}]$. (b) Cartoon representation of the Ag_5Pd_4 cluster with its ligands.

We believe that the peak at m/z 2839 is the molecular ion and others are fragments due to the following reason. Even when the cluster is stable, fragmentation is common under ESI conditions. For example, the stable $Au_{25}(SR)_{18}$ cluster shows a fragment in the mass spectrum due to the $Au_4(SR)_4$ loss.⁵² Even the stable $Ag_{44}(SR)_{30}$ cluster, for which the crystal structure was determined recently,^{35,36} shows several fragments due to $Ag_m(SR)_n$ losses. It is important to mention here that for this cluster the molecular peak with 4- charge has much lower intensity compared with the fragments seen in the lower mass range $(m/z \ 100-1500)$.³² Au₂₅ and Ag₄₄ are the most stable clusters reported so far, for the case of gold and silver, respectively. They have closed-shell electronic configuration consisting of 8 and 18 number of electrons. These clusters show stable species in the gas phase along with their fragments. So, it is clear that fragmentation is likely under ESI conditions for clusters. However, the peak at m/z 2839 is very likely to be an intact ion as no other ion was seen in the higher mass region, until m/z 20 000. Spectrum was also measured at various ESI conditions, which ensured that no other higher mass molecules are present in the solution. No higher charge state was detected. All of these suggest that the peak at m/z2839 is the molecular ion and the cluster in solution state itself is negatively charged. We have focused only on cluster 2 in this report because it gives a well-defined and fully assignable mass spectrum. Subsequent studies were done only on this cluster. The cluster is stable for more than one month under ambient conditions.

For a detailed understanding of the fragmentation pattern and for structural elucidation, tandem mass spectra were measured for each peak present in the mass spectrum of cluster 2. The most intense and closest peak obtained in MS^2 was subjected to further fragmentation to get the MS³ data, and subsequent MSⁿ measurements were performed until reasonable intensities were seen. Although there is no particular pattern followed for each fragmentation, we could see four different types of losses overall; they correspond to -SePh, -Ph, Ag, and Pd. Sometimes, simultaneous losses of -SePh and -Ph as well as Ag/Pd and -SePh were seen. The MS/MS data for the peak at m/z 2839 shows (Figure 3) an initial loss of m/z 312, followed by a loss of m/z 624 that correspond to 2 and 4 SeR (R = C_6H_5) moieties, respectively. MS³ was performed with the fragment at m/z 2525 (assigned to $Ag_5Pd_4(SePh)_{10}$, as previously discussed. Interestingly, all of the fragments seen in Figure 2 for the parent clusters are also

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Figure 3. MS/MS data of m/z 2839. Repeated MS/MS was done with the most intense fragments closer to the parent ion (marked by gray star in all traces, except the last one). Multiple losses were seen for each case, and they are indicated on the arrow. Up to MS⁹ was achievable with reasonable intensity. Spectra have been shifted vertically for clarity.

present here but with low intensity. Repeated MS/MS data were taken with the most intense and the closest fragment of the parent ions, and, surprisingly, MS^9 was achievable. This is the maximum limit of MS/MS studies of clusters reported so far. The fragmentation pattern observed is shown in Figure 3. In MS^9 , after fragmentation, the stable species generated is of composition $[Ag_3Pd_3(SePh)_3Se]^-$, which has a $Ag_3Pd_3^-$ core. More importantly, here also we did not see any further fragmentation, suggesting that the $Ag_3Pd_3^-$ core is highly stable.

MS/MS of the fragment at m/z 2604 was also studied (Figure S6 in the Supporting Information), and for this case, successive ligand losses were seen and the metal core remains intact throughout. MS^2 of $[Ag_5Pd_4(SePh)_{10}Se]^-$ produces two new peaks due to consecutive losses of two units of (SeR+R), part of the ligand. Mass difference for the fragments obtained from MS³ of the peak at m/z 2374 corresponds to the losses of two units of selenium and one R. Similar trends have been observed for MS⁴ and MS⁵ also. In this process, five units of SeR and two units of R have been lost from the parent species, and the cluster was left with a probable composition, $[Ag_5Pd_4(SePh)_3Se_3]^-$. Because of poor intensity, beyond MS⁵ was not achievable. Tandem MS of the peak at m/z 2204 due to $[Ag_3Pd_3(SePh)_{10}]^-$ also shows similar fragmentation pattern, as seen for the previous case (Figure S7 in the Supporting Information). It loses a total of seven units of SeR and one unit of R keeping the metal part intact. Finally, it gives the daughter ion having a probable composition, [Ag₃Pd₃(SePh)₂Se]⁻, which further supports the high stability of the Ag₃Pd₃⁻ core. Detailed fragmentation patterns have been illustrated in Figure S7 in the Supporting Information. Because silver and palladium are close in their atomic masses, the presence of Pd in the cluster ions should be ensured. This was thought to be accomplished by tandem mass spectrometry, utilizing the isotope distribution of elements (107 Ag (51.8%), 109 Ag (48.2%), 102 Pd (1.0%), 104 Pd (11.2%), 105 Pd (22.3%), 106 Pd (27.3%), 108 Pd (26.5%), and ¹¹⁰Pd (11.7%); abundances are given as percentages). The parent ion at m/z 2839 was selected that contains an envelope

of 31 detectable peaks with unit mass difference, ranging from m/z 2823 to 2853. Initially, MS/MS was taken for the peak at m/z 2839 with the given isotope width of 30. This corresponds to the parent ion selection with a width of 15 mass units on either side of m/z 2839. As expected, it will generate the corresponding fragments with similar isotope width (one of the fragments at m/z 1904 has been shown in Figure 4A). In the second case, each of the 31 peaks of the parent ion (ranging from 2823 to 2853) has been selected for MS/MS studies with an isotope width of 1. Here each peak was chosen with a width of 0.5 mass unit on each side. In most cases, several (more than 6) peaks were seen in the MS/MS spectrum with varying intensities which are expected from the isotope pattern of palladium. One such MS/MS spectrum taken with unit isotope width is shown in Figure S8 in the Supporting Information. The cumulative envelope shown in Figure 4A can be generated by accumulating all of the individual MS/MS spectra taken with unit isotope width (Figure 4B). A computational analysis has been done (Table S1, details of the method used are in Supporting Information 1) to predict the assignment of each peak responsible for this MS/MS data (with a maximum at m/z1905) through a home-built software. As can be seen, although each peak is composed of multiple combinations of Pd and Ag isotopes, a complete analysis of the positions and intensities is possible, confirming the alloy composition (Figure S9 in the Supporting Information). The mass assignment is complicated as the number of combinations contributing to the peaks is ~465 million (see Computational details in Supporting Information 1 for a discussion), and suitable truncation has to be done to relate to the observed mass peaks. Isotope combinations of the peaks of maximum abundances are shown in Figure S9 in the Supporting Information. Other ions have also been investigated by tandem MS.

It is also important to mention here that this composition is one in which ligands are more than the core atoms and such structures are less common. However, recent crystal structures of silver clusters (such as $[Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8]^{29}$ and $[Ag_{16}(DPPE)_4(SC_6H_3F_2)_{14}])^{53}$ suggest that such ligand-excess



Figure 4. MS/MS spectrum showing a fragment derived from m/z 2839. "A" and "B" are the MS/MS data derived from m/z 2839 with the isotope width of 30 and 1, respectively. Trace B is composed of a number of MS/MS spectra. Each peak selected for MS/MS studies (m/z 2823 to 2853, shown on top of the spectra) and the resulting fragments is shown using specific colors.

structures are also possible. It was also shown that silver can coordinate with three sulfur ligands. It is important to note that Pd(II) can coordinate with four ligands. So, it is not unusual to see the existence of such clusters.

HRTEM of cluster 2 (Figure 1b) shows the presence of highly monodisperse clusters with an average diameter of 0.85 nm (Figure 1c). Complete absence of bigger particles suggests the high purity of the cluster. The composition was further supported with SEM/EDAX data, where the Ag:Pd:Se ratio matches well with the calculated one (Figure S10 in the Supporting Information). Precise composition was already confirmed by HRESI MS data. The EDAX data were to support the suggestion. XPS survey spectrum shown peaks (Figure S11A in the Supporting Information) for all expected elements. The Ag $3d_{5/2}$ peak could be fitted to two components (Figure S11B in the Supporting Information) with maxima at 367.5 and 368.0 eV binding energy (BE). The Pd $3d_{5/2}$ peak appeared at a BE of 336.6 eV, which lies in b etween the values of Pd(II) and Pd(0) (Figure S11D in the Supporting Information).⁵⁴ The Se 3d peak came at 54.3 eV BE (Figure S11C in the Supporting Information), as expected for the selenolate species. It is important to mention here that Ag(0) and Ag(I) have only 0.5 eV⁵⁵ difference in binding energy, so it is difficult to predict the exact charge on silver from photoemission data. However, the data suggest that Ag is present in two oxidation states with 3:2 ratio, whereas Pd is closer to its Pd(II). Although it is difficult to propose a structure based on this information alone, it is likely that distinct silver forms exist in the cluster.

Outer electron count of the $Ag_5Pd_4(SePh)_{12}$ system would suggest a 33 electron species (taking s¹ and d¹⁰ valence shells for Ag and Pd, respectively, and subtracting one electron each for the ligands, which form the selenolates, and the entity as a whole may be stabilized by a negative change, making the system a closed shell. This may be the reason for the larger intensity of the negative ion. However, a clear rationalization of the data would require the structure.

In summary, selenolate-protected Ag–Pd alloy clusters have been synthesized using one-pot solution-phase synthesis. The crude cluster was purified using HPLC, which gave three different clusters with characteristic optical absorption spectra. ESI MS data suggest that only cluster **2** shows interesting features for which the molecular ion peak appeared at m/z2839, assigned as $[Ag_5Pd_4(SePh)_{12}]^-$. Systematic MS/MS was carried out for the molecular ion peak as well as other fragments. Interestingly, up to MS⁹ is achievable with reasonable intensity, which is the maximum limit for a monolayer-protected cluster reported so far. The result is also supported by several other characterization measurements. It is hoped that single-crystal studies will be possible once its stability is improved.

EXPERIMENTAL METHODS

Materials used in the synthesis are listed in the Supporting Information.

Synthesis of Ag_SPd_4 Cluster. One-pot solution phase route was followed to synthesize the crude cluster. Silver trifluoroacetate (10 mg) and sodium tetracholopalladate (7 mg) were dissolved in 36 mL of acetonitrile taken in a conical flask and kept for string. Then, 5 μ L of benzeneselenol was added and the color changed from faint yellow to orange, confirming the formation of selenolate. Finally, 10.2 mg of sodium borohydride (s) was added and stirring was continued for 2 h. The color changed to yellowish brown, which confirmed the formation of the crude cluster. It was then centrifuged at 5000 rpm, and the centrifugate was collected for HPLC purification.

Materials, methods, and computational details are given in Supporting Information 1.

ASSOCIATED CONTENT

S Supporting Information

Details of materials, XPS, SEM/EDAX, ESI MS, and MS/MS data of Ag_5Pd_4 clusters. Photographs, UV/vis, and ESI MS data of crude and isolated clusters, individual peak assignments of a MS/MS fragment, and a table of assignments of an MS/MS fragment. 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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