J|A|C|S
COMMUNICATIONS

Published on Web 09/07/2010

# Glutathione-Stabilized Magic-Number Silver Cluster Compounds

Santosh Kumar, Michael D. Bolan, and Terry P. Bigioni*

*Department of Chemistry, The University of Toledo, Toledo, Ohio 43606*

Received July 1, 2010; E-mail: Terry.Bigioni@utoledo.edu

***Abstract:*** Magic-number theories, developed to explain the anomalous stability of clusters in the gas phase, are being successfully applied to explain the stability of families of condensed phase Au clusters. To test the generalizability of these theories, we have synthesized a family of magic-numbered Ag clusters. Silver clusters ligated with glutathione (GSH) were synthesized by reduction of silver glutathiolate in water and then separated by polyacrylamide gel electrophoresis (PAGE). The raw synthetic product consisted of a family of discrete Ag:SG clusters, each forming a band in the PAGE gel. Varying reaction conditions changed the relative abundance of the family members but not their positions and colors within the gel, indicating the molecular precision of magic-number clusters. Absorption onsets for the most abundant clusters monotonically decreased with increasing cluster size, and spectra contained a small number of peaks that corresponded to single electron transitions. Although these Ag:SG clusters are related to Au:SG clusters, the distribution of cluster sizes and the optical absorption spectra were markedly different for the two families. This suggests that the Ag:SG clusters are not a simple extension of the Au:SG system, possibly due to differences in Au and Ag chemistry. Alternatively, condensed-phase magic-number cluster theories may need to be more complex than currently believed.

Small Au clusters have provided an opportunity to explore the rules for nanostructure stability.[1−11] This work has been based upon gas phase experiments that showed that geometric and electronic shell closings led to the anomalous stability of "magic-number" clusters.[12,13] Herein we report our efforts to test the generality of these rules for nanostructure stability by synthesizing a family of magic-numbered Ag clusters.

It has been shown that small gold clusters, perhaps too small to be called nanoparticles, are indeed synthesized as a family of magic-numbered clusters.[2,3] Electrospray ionization mass spectrometry (ESI-MS) was used to determine the chemical formulas of each member of the family of glutathione-ligated Au clusters and has shown that the clusters always occur with the same formulas.[4] Work on understanding the electronic and atomic structures of this class of clusters has accelerated, including the complete structural determination of a 25, 38, and 102 atom Au clusters.[8−11]

Both Au and Ag are noble, free electron metals and have almost identical bulk lattice constants. Based on these similarities, Ag could be expected to follow the same shell closing rules as Au. The shell closing rules for Ag remain untested, however. In the present study, we show that it is possible to synthesize a family of discrete-sized Ag clusters that are protected by a ligand shell of glutathione (GSH). The synthesis and subsequent separation produced as many as 21 distinct Ag:SG species, with strikingly different optical properties. These results are the first clear evidence for Ag magic-number clusters and allow for a direct comparison with Au magic-number clusters.

Clusters were synthesized by reducing silver thiolates[14] with $NaBH_4$ in the presence of excess GSH. Colorless thiolate solids were formed immediately upon mixing aqueous $AgNO_3$ and GSH. This is analogous to Au(I)SR polymer formation in the Au nanoparticle syntheses.[15] Slow addition of $NaBH_4$ led to the reduction of the silver thiolates, eventually producing a deeply colored solution of Ag:SG clusters. As the clusters grew, the solution color changed from yellow to orange to brown and then almost black, indicating a size dependence for the color. The reaction produced no insoluble material.

The raw product was separated using polyacrylamide gel electrophoresis (PAGE). At least 16 discrete bands emerged from the mixture, as shown in Figure 1. The finest bands were better discerned at higher loadings (inset of Figure 1A). The colors varied from band to band, which suggests that this family of Ag:SG clusters consists of chemically distinct species. At least 5 additional bands were identified from a synthesis that used less glutathione and produced higher mass clusters (Figure 1B). In total, 21 distinct bands were discernible by the naked eye.

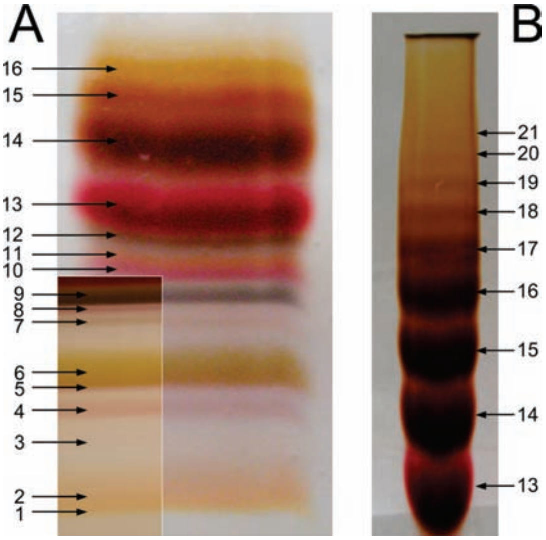

***Figure 1.*** PAGE results for Ag:SG clusters. (A) Bands of discrete Ag:SG clusters. The smallest clusters are at the bottom and have the lowest index. Inset: finer bands revealed at a higher concentration. (B) Discrete higher-mass clusters, synthesized with less glutathione.

Scanning transmission electron microscopy (STEM) imaging of the product confirmed the presence of very small Ag particles, ∼1 nm in diameter, surrounded by organic material. Few large nanoparticles were found. Small-angle powder X-ray diffraction revealed a particle size of about 2.5 nm, which is consistent with the STEM results plus the ligand shell. Energy dispersive X-ray spectroscopy (EDS) confirmed the presence of Ag and S, and NMR confirmed the existence of glutathione in the purified sample. NMR

10.1021/ja105836b

spectra were consistent with signatures previously attributed to metal-bound ligands.[15]

Different synthesis conditions were able to change the overall composition of the raw product but did not change the component clusters. For example, changing the solvent composition, Ag:GSH ratio, and reduction rate shifted the mass distribution toward either larger or smaller cluster sizes (see Supporting Information), while the relative positions and colors of the PAGE bands were independent of reaction conditions. The pattern and colors of the bands were always reproduced with only variations in their abundance, strongly suggesting the molecular precision of magic-number clusters.

The similarities between Au and Ag allow comparisons to be made between the patterns of PAGE bands for each family of clusters. Both Au and Ag contribute one free electron per atom to the clusters, so the same pattern of *electronic* shell closings as a function of the number of core atoms is expected for each metal. Further, the atomic sizes and alkyl thiol packing densities are almost identical for bulk Au and Ag.[16] The same pattern of *atomic* shell closings is therefore expected, and the charge and electrophoretic mobility for the same size clusters should also be similar. A similar pattern of bands is therefore expected.

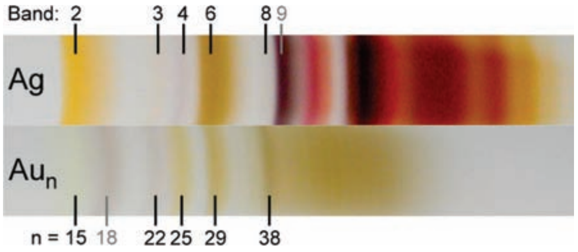

***Figure 2.*** Ag:SG and Au:SG bands from the same PAGE gel, using concentrations of 15 and 30 mg/mL, respectively. The number of atoms in each Au:SG band is indicated.[4]

The patterns of bands for Au and Ag clusters run on the same gel are shown in Figure 2. Although there is some correspondence between individual bands, it is immediately apparent that the mass distribution is quite different for the two families of clusters. This suggests that the most stable structures may be different since the most abundant Au:SG and Ag:SG clusters are not necessarily the same size. This could be due to a difference in Au−S and Ag−S chemistry, or it could indicate a need to consider new models.

There are also striking differences in the optical properties of Au and Ag clusters. The optical density of Ag is significantly higher than that of Au, as can be seen in Figure 2. The integrated spectrum (280−1100 nm) of the raw Ag:SG mixture was almost double that of Au:SG (see Supporting Information). The absorption spectra of the Ag bands are also quite different compared with Au:SG clusters.[4] The Ag spectra are less complex, containing a few well-defined peaks as well as more subtle features, as shown in Figure 3 and Table 1.

Closed electronic shells lead to large HOMO−LUMO gaps, which impart stability to clusters and can be observed as high-energy absorption onsets in optical spectra. The measured onset energy for light absorption decreases monotonically with increasing Ag:SG cluster size (Table 1), as might be expected based on quantum mechanical or statistical arguments.[17] The position of the first identifiable peak changes nonmonotonically, however, as might be expected based on electronic shell closings and particle symmetry.

The stability of Ag:SG clusters was excellent in dry powder form. PAGE results showed no significant differences between freshly prepared clusters and powder stored in air for 8 months. Stability in aqueous solution was size dependent, however. While the smallest particles appeared to be stable, bands 14 and higher were lost after ∼1 day in aqueous solution. This is consistent with the idea that smaller clusters would have enhanced stability due to their larger HOMO−LUMO gaps. All cluster sizes were stable within the gel.

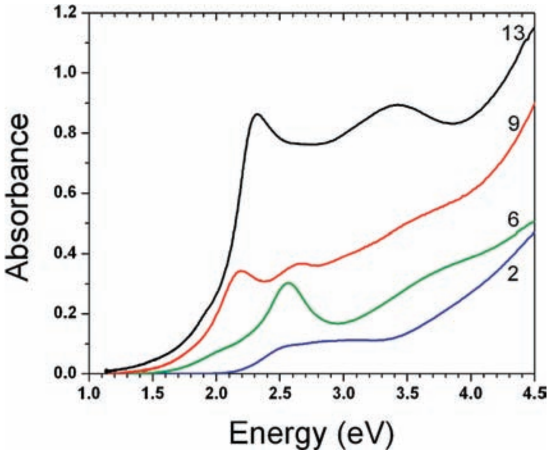

***Figure 3.*** Optical absorption spectra of four selected Ag:SG bands, as labeled, chosen based on abundance and the quality of separation. Spectra were taken of clusters inside the gel.

***Table 1.*** Salient Features in the Optical Spectra[a]

| | Abs. onset (eV) | first peak (eV) | second peak (eV) | third peak (eV) |
|---|---|---|---|---|
| band 2 | 2.1 | 2.51 | 2.82 | 3.12 |
| band 6 | 1.6 | 2.01 | 2.55 | 3.75 |
| band 9 | 1.3 | 2.18 | 2.65 | 3.70 |
| band 13 | (1.0) | 1.90 | 2.32 | 3.42 |

[a] Parentheses indicate estimate by extrapolation.

In conclusion, we have demonstrated the existence of a family of small glutathione-ligated Ag clusters. The appearance and properties of each family member was independent of reaction conditions, consistent with the molecular precision of magic-number clusters. Although these Ag:SG clusters are related to Au:SG clusters, they are not a simple extension of the Au model. This suggests that the rules for determining the most stable structure could be different for Ag:SG, due to differences in Au and Ag chemistry. Alternatively, condensed-phase magic-number cluster theories may need to be more complex than currently believed.

**Acknowledgment.** The authors would like to thank Drs. Don Ronning and Robert Whetten for useful discussions and Ms. Vidhi Mishra and Mr. Anil Desireddy for their kind assistance.

**Supporting Information Available:** Synthetic methods, PAGE, UV−vis, XRD, STEM, EDS, and NMR results. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428–433.
(2) Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2000**, *104*, 2630–2641.
(3) Negishi, Y.; Takasugi, Y.; Sato, S.; Yao, H.; Kimura, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2004**, *126*, 6518–6519.
(4) Negishi, Y.; Nobusada, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 5261–5270.
(5) Negishi, Y.; Chaki, N. K.; Shichibu, Y.; Whetten, R. L.; Tsukuda, T. *J. Am. Chem. Soc.* **2007**, *129*, 11322–11323.
(6) Akola, J.; Walter, M.; Whetten, R. L.; Häkkinen, H.; Grönbeck, H. *J. Am. Chem. Soc.* **2008**, *130*, 3756–3757.

(7) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 9157–9162.
(8) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. *J. Am. Chem. Soc.* **2008**, *130*, 3754–3755.
(9) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. *J. Am. Chem. Soc.* **2008**, *130*, 5883–5885.
(10) Qian, H.; Eckenhoff, W. T.; Zhu, Y.; Pintauer, T.; Jin, R. *J. Am. Chem. Soc.* **2010**, *132*, 8280–8281.
(11) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. *Science* **2007**, *318*, 430–433.
(12) deHeer, W. A. *Rev. Mod. Phys.* **1993**, *65*, 611–676.
(13) Martin, T. P. *Phys. Rep.* **1996**, *273*, 199–241.
(14) Dance, I. G.; Fisher, K. J.; Herath Banda, R. M.; Scudder, M. L. *Inorg. Chem.* **1991**, *30*, 183–187.
(15) Schaaff, T. G.; Knight, G.; Shafigullin, M. N.; Borkman, R. F.; Whetten, R. L. *J. Phys. Chem. B* **1998**, *102*, 10643–10646.
(16) Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 9389–9401.
(17) Wyrwas, R. B.; Alvarez, M. M.; Khoury, J. T.; Price, R. C.; Schaaff, T. G.; Whetten, R. L. *Eur. Phys. J. D* **2007**, *43*, 91–95.

JA105836B