

Synthesis and Structural Characterization of an Atom-Precise Bimetallic Nanocluster, $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$

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Supporting Information

ABSTRACT: A bimetallic ligand-protected cluster, $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$ (DMSA = *meso*-2,3-dimercaptosuccinic acid) was synthesized and characterized through electrospray ionization mass spectroscopy. Such bimetallic clusters involving a noble metal and a first-row transition metal have not been previously reported. Theoretical calculations revealed an octahedral structure with silver atoms occupying the corners of the square plane and the nickel atoms at the apexes. Close agreement between the predicted and observed spectroscopic features was found.

Metal nanoclusters composed of a small but precise number of atoms are of fundamental importance for investigating the evolution of the structure and physicochemical properties in going from the atomic state to the metallic state.¹ In addition, such nanoclusters are of interest because of their unique stability¹ and unusual optical² and catalytic properties.³ These properties differ from those of larger nanoparticles and result from quantum confinement effects associated with the small sizes of the clusters (typically <2 nm).⁴ A great deal of research has gone into thiolated clusters of gold and silver because of the stability afforded by the strength of the metal–sulfur bond and the resistance of these metals to oxidation.⁵ Much of this research has focused on the tunability of the properties as a function of the number of atoms within a cluster⁶ or the ligand used.⁷ Bimetallic ligand-protected clusters offer an additional degree of freedom, as the clusters' properties may be controlled via compositional tuning. The few previously synthesized monodisperse bimetallic clusters include $(\text{AuAg})_{144}(\text{SR})_{60}$,⁸ $\text{Ag}_x\text{Au}_{25-x}\text{SR}_{18}$,⁹ $\text{Au}_7\text{Ag}_6\text{SR}_{10}$,¹⁰ and $\text{PdAu}_{24}\text{SR}_{18}$.¹¹ Notably, in all of the currently reported examples of thiol-protected bimetallic clusters, the two metals involved also form stable alloys in the bulk. The seemingly enhanced stability of bimetallic clusters involving alloyable metals may be a contributing factor to the relatively poor diversity of such clusters. Particularly noteworthy is the absence of known atomically precise bimetallic thiolated clusters combining the commonly employed noble metals with first-row transition metals, despite numerous theoretical investigations into such clusters.¹² Several silver- and nickel-containing metal–thiolate complexes have been reported; however, these do not contain a multimetallic core.¹³ Herein we report the wet-chemical synthesis and structural determination of a Ag_4Ni_2 cluster protected by the ligand *meso*-2,3-

dimercaptosuccinic acid (DMSA). Since poor miscibility prevents silver and nickel from forming alloys in the bulk,¹⁴ this cluster represents an important step toward increased metal diversity in well-characterized bimetallic clusters. To the best of our knowledge, this is also the first report of a thiolate-protected cluster containing both a noble metal and a first-row transition metal.

One methodology for the preparation of bimetallic clusters is to modify well-established syntheses of homometallic analogues.^{9,11} $\text{Ag}_7(\text{DMSA})_4$ clusters have been synthesized and studied by several groups since being reported by Wu and co-workers.⁵ The bimetallic Ag_4Ni_2 cluster was synthesized by a modification of the above synthetic procedure. In a typical experiment [for additional details, see the Supporting Information (SI)], nickel nitrate hexahydrate (26.2 mg, 0.09 mmol) and silver nitrate (86.6 mg, 0.51 mmol) were dissolved in 60 mL of deoxygenated ethanol. The solution was chilled to 0 °C with an ice bath, and then DMSA (108.0 mg, 0.57 mmol) was added with slow stirring, resulting in a yellowish green suspension. Following DMSA addition, the flask was sealed and purged with nitrogen. After the reaction mixture was allowed to equilibrate for 4 h, a solution of sodium borohydride (46.5 mg, 1.23 mmol in 5 mL of EtOH) was injected slowly over several minutes under vigorous stirring. The solution was allowed to react overnight, during which time the temperature was allowed to rise to ambient level. The resultant cloudy brown suspension was centrifuged from solution and washed with methanol and ethanol. The solids were dried under a nitrogen flow, dissolved in water, and centrifuged to remove any remaining insoluble material. The supernatant was removed, and the desired cluster was precipitated by the addition of ethanol. The cluster was dried and purified by native polyacrylamide gel electrophoresis (PAGE), affording a green solid (~22% yield based on Ni) that was used in characterization experiments.

The identity of the cluster was assessed by mass spectrometry and elemental analysis. Electrospray ionization mass spectrometry of the cluster gave rise to a series of peaks because of the distribution of various isotopes. Our sample showed two prominent cluster peaks centered at m/z 633.7 $[\text{M} - 2\text{H}]^{2-}$ and m/z 422.1 $[\text{M} - 3\text{H}]^{3-}$ (Figure 1 inset). Several additional smaller peaks resulting predominantly from sodium or tris exchange with DMSA carboxylic acid protons were

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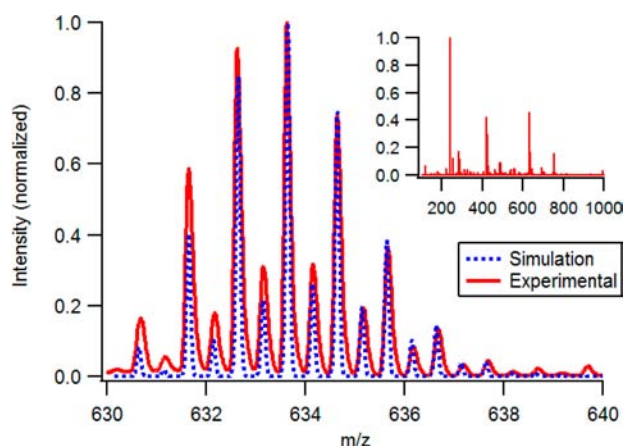


Figure 1. Experimental mass spectrum of the $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$ cluster overlaid with a simulation¹⁵ of the peak positions and isotope distribution. The inset shows a zoomed-out spectrum.

observed at higher m/z . An examination of possible clusters with a mass of 1269.4 amu and having the formula $\text{Ag}_x\text{Ni}_y(\text{DMSA})_z$ indicated $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$ to be a likely possibility. Comparison of the experimental peak position and isotope distribution to a simulated mass spectrum of $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$ showed an excellent match (Figure 1).¹⁵ More detailed mass spectra with peak identifications are given in Figures S1–S3 in the SI. MS/MS experiments (Figure S2) revealed a $\text{Ag}_4\text{Ni}_2\text{S}_4$ fragment consistent with a rearrangement similar to the McLafferty rearrangement, which cleaves one C–S bond and one S–metal bond (Figure S4), implying a core of $\text{Ag}_4\text{Ni}_2\text{S}_8$.¹⁶ Elemental analysis performed on the cluster via inductively coupled plasma atomic emission spectroscopy determined a Ag:Ni:S ratio of 1.0:0.56:2.6, compared with an expected ratio of 1.0:0.50:2.0. The abundance of sulfur may result from minor cluster decomposition during electrophoretic separation.

As the purity of the synthesized cluster was difficult to confirm by mass spectrometry alone, additional evidence of monodispersity was obtained. The appearance of a well-defined band upon running the PAGE (Figure 2A inset) provided strong evidence of a single species within that band, given the ability of PAGE to separate even very similar clusters.¹⁷ The well-defined peak at 328 nm in the UV–vis spectrum (Figure 2A) also provided evidence of high purity. The possibility of larger clusters was discounted on the basis of the lack of precipitates or color gradients observed after prolonged high-speed centrifugation.

The synthesized clusters were highly soluble in water and could tolerate limited oxygen exposure while in solution. Solutions of clusters stored under nitrogen showed good stability, as determined by time-resolved optical spectroscopy (Figure S5). In the solid state, the cluster appeared to be quite stable regardless of oxygen exposure and could be stored for weeks with no apparent change in color or sample integrity.

Theoretical investigations using gradient-corrected density functional theory¹⁸ were performed to determine the structure of the $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$ cluster. The lowest-energy structure identified is shown in Figure 3 along with the respective Hirshfeld atomic charges. Additional isomers are shown in Figure S6. In the lowest-energy structure, the four Ag and two Ni atoms form a distorted octahedral structure, and the sulfur atoms decorate each of the Ag–Ni vertices. This lowest-energy

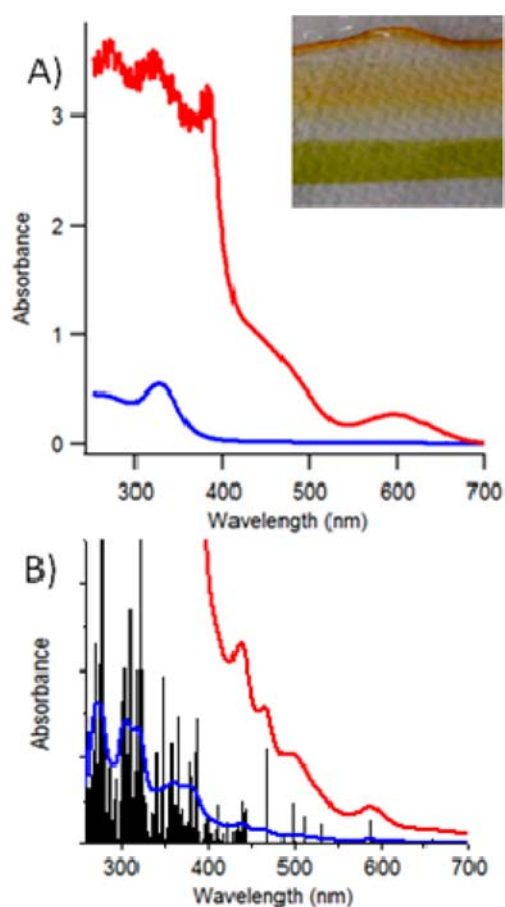


Figure 2. (A) Experimental UV–vis spectra for $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$ in deoxygenated water. The solution for the red spectrum was 40 times more concentrated than that for the blue spectrum; together, the spectra show both strong and weak absorptions. The inset shows PAGE separation of the green $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$ cluster from side products. (B) Simulated UV–vis spectra for $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$. The red spectrum is 10 times the blue spectrum; the black lines indicate the oscillator strengths of specific transitions.

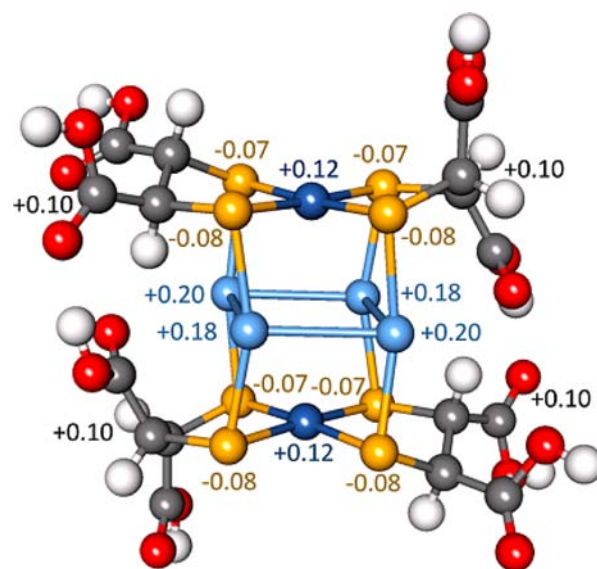


Figure 3. Proposed structure of $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$. Hirshfeld atomic charges on the Ag, Ni, and S atoms and the remainder of the ligands are shown.

structure contains eight S–Ni bonds and eight S–Ag bonds.¹⁹ The density of states for the cluster (Figure S7) has a HOMO–LUMO gap of 1.28 eV. The structure is nonmagnetic because the sulfur atoms are in a square planar configuration around the Ni atoms and split the 3d orbitals to produce a low spin 3d⁸ configuration with a large gap between frontier orbitals that are localized on the Ni atoms. This is consistent with experimental magnetic data obtained using a superconducting quantum interference device (SQUID), which showed an extremely low magnetic moment (Figure S8). The presence of this very small magnetic signal is likely attributable to nickel ions formed from cluster decomposition or other magnetic impurities.

The Ag₄Ni₂(DMSA)₄ cluster is stabilized by charge transfer from the Ag atoms to the Ni(DMSA)₂ complex that serves as a precursor. Isolated Ni(DMSA)₂ is a square-planar complex (Figure S9) with triplet multiplicity. The binding energies of DMSA are 4.58 eV for the first ligand and 3.28 eV for the second ligand, while the binding energy of DMSA to Ag is 2.01 eV. The binding energy of DMSA is much larger with Ni than with Ag, so the DMSA binds to Ni preferentially. While the Ni(DMSA)₂ complex is the most stable precursor, it is deficient by two electrons and has an open electronic shell. Thus, four Ag atoms are needed to stabilize the two Ni complexes. The Ag atoms donate charge to the Ni producing a bimetallic cluster with significant charge transfer from the Ag atoms to the Ni atoms to produce a closed electronic shell, as demonstrated by the 1.28 eV HOMO–LUMO gap of the cluster. Figure S10 shows a fragment analysis of the bonding between the Ni(DMSA)₂ complexes and the Ag atoms, with the 3d_{xz} and 3d_{yz} orbitals of Ni being completely filled only after the incorporation of the Ag atoms. The combination of electronic factors (with four Ag atoms needed to close the electronic shell) and geometric factors (in which the number of Ag–S bonds is maximized by the octahedral arrangement) explains why the Ag₄Ni₂(DMSA)₄ cluster is stable.

To provide additional confirmation for the predicted structure, the absorption spectrum of the cluster was calculated using time-dependent density functional theory. The calculated optical spectrum (Figure 2B) shows reasonable agreement with the experimental spectrum. We calculated the first significant absorption to be at 590 nm, consistent with the weak absorption peak observed at 600 nm. This is the 13th excited state of the cluster and corresponds to the transition between the HOMO–6 and LUMO+1 (Figure S11). One potential isomer in which the Ag₄Ni₂S₈ core is nearly identical but the DMSA ligands are staggered rather than eclipsed (isomer 2 in Figure S6) was found to be 0.61 eV higher in energy. This isomer was calculated to have a strong absorption at 452 nm (Figure S12), which was not observed in the experimental spectrum, so we infer that the structure in Figure 3 is the predominant species. A third possible isomer in which the Ni atoms are adjacent to each other was computed to be 0.82 eV higher in energy and to have a strong absorption at 700 nm. The lowest-energy structure coupled with the agreement between the experimental and theoretical absorption spectra confirms our assignment.

In conclusion, we have reported the synthesis, isolation, and structural characterization of a bimetallic ligand-protected cluster, Ag₄Ni₂(DMSA)₄. The cluster can be synthesized in large quantities, is stable in aqueous solution, and has partially exposed silver and nickel sites, making it a promising species for additional studies of catalytic properties. Additionally, as is evident from the MS/MS experiments, the cluster may be

employed as a precursor to atom-precise bimetallic sulfides, such as Ag₄Ni₂S₄.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis and characterization details, mass spectra with detailed peak assignments, MS/MS fragmentation mechanism, time-dependent UV–vis spectra, details and figures for theoretical calculations, magnetic data, and calculated optical transitions and absorption spectra. 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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