Superatoms

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$[Ag_{21}\{S_2P(O\textit{i}Pr)_2\}_{12}]^+$: An Eight-Electron Superatom[**]

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Abstract: *A novel discrete $[Ag_{21}\{S_2P(OiPr)_2\}_{12}](PF_6)$ nanocluster has been synthesized and characterized by single-crystal X-ray diffraction and also NMR spectroscopy (^1H, ^{31}P), ESI mass spectrometry, and other analytic techniques (XPS, EDS, UV/Vis spectroscopy). The Ag_{21} skeleton has an unprecedented silver-centered icosahedron that is capped by eight additional metal atoms. The whole framework is protected by twelve dithiophosphate ligands. According to the spherical Jellium model, the stability of monocationic nanocluster can be described by an 8-electron superatom with $1S^2 1P^6$ configuration, as confirmed by DFT calculations.*

Noble-metal nanoparticles have been extensively used for various applications in numerous fields, such as catalysis, energy conversion, sensing, electronics, photochemistry, and medicine.[1–5] Among the coinage metals (Cu, Ag, Au), the family of gold nanoclusters stabilized by phosphine/thiol type ligands and fully characterized at the molecular level constitute a well-known and important class of noble-metal nanoparticles.[6,7] Recently, thiolate-protected anionic silver and silver–gold intermetallic nanoclusters, formulated as $[M_{12}Ag_{32}(SR)_{30}]^{4-}$ (M = Ag, R = *p*-mercaptobenzoic acid (*p*-MBA); M = Ag, Au, R = PhF, PhF_2, $PhCF_3$), have been characterized independently by Bigoni and co-workers using (*p*-MBA),[8] and Zheng et al. using fluorinated aryl thiol ligands.[9] The unique solid-state structure of these Ag_{44} clusters shows an empty Ag_{12} icosahedron enclosed within a concentric Ag_{20} dodecahedron, this whole 32-atom core being protected by six $Ag_2(SR)_5$ units.[10] Their unusual stability has been attributed to the closed-shell 18-electron cluster count within the unified superatom model concept based on the spherical Jellium model.[11] Furthermore, crystal structures of silver (Ag^I/Ag^0) nanoclusters, Ag_{14}, Ag_{32}, and Ag_{34} stabilized by both thiolate and phosphine ligands have been reported.[12] As the synthesis of these silver nanoclusters includes a hydride source $[BH_4]^-$, the possibility of hydride encapsulation inside the M_{12} icosahedron has been discussed by Teo.[13] According to Teo's propositions, two series of hydride-containing closed-shell Jellium-type clusters could arise: the 18-electron series $[H_xAg_{44}(SR)_{30}]^{(4-x)-}$ and the 20-electron series $[H_xAg_{44}(SR)_{30}]^{(6-x)-}$ ($x = 0,1,2$). Thus, it will be of topical interest to structurally characterize more thiolate-protected silver nanoparticles having a magic number electron count to address the possibility; that is, whether hydride is present within the nanoclusters or not.

Over the years, we have fabricated a series of air- and moisture-stable silver(I) hydride cluster compounds $[Ag_7HL_6]$, $[Ag_8HL_6]^+$, and $[Ag_{11}HL_9]^+$ stabilized by bridging dichalcogen donor ligands (L).[14,15] Dithiolate-protected silver subnanoclusters have been proposed as intermediates in silver nanoparticles synthesis by utilizing hydrido silver clusters as the precursors.[14d] Adopting a new strategy which can significantly expand a cluster nuclearity from 8 to 28 in copper systems by the treatment of excess amount of borohydride in the presence of dichalcogen ligands,[16] we report herein a new dithiolate-protected silver nanocluster formulated as $[Ag_{21}\{S_2P(O\textit{i}Pr)_2\}_{12}](PF_6)$, (**1**), which has eight cluster electrons in agreement with the unified superatom concept. This structure consists of a centered icosahedron Ag_{13} core that is further capped by eight silver atoms and stabilized by 12 dithiophosphate ligands (dtp; $\{S_2P(O\textit{i}Pr)_2\}^-$). To the best of our knowledge, the core unit of this nanocluster is the first example of silver-centered Ag_{12} icosahedron,[17] even though a metal-centered icosahedron is known with other noble metals, such as palladium[18] and gold,[19,7c] and more importantly embedding a silver atom inside an icosahedron Ag_{12} shell has been a topical project in contemporary theoretical calculations.[20]

The synthesis of $[Ag_{21}\{S_2P(O\textit{i}Pr)_2\}_{12}]^+$ involved $NaBH_4$ reduction of $[Ag(CH_3CN)_4](PF_6)$ in the presence of $(NH_4)[S_2P(O\textit{i}Pr)_2]$ ligands following a one-phase method using THF as the solvent. The growth of single crystals was performed by vapor diffusion of hexane into a concentrated acetone solution of the as-synthesized nanoclusters at 4 °C. Rectangular-shape dark crystals of **1** were obtained in a couple weeks. Its unique structure was analyzed by single-crystal X-ray crystallography and the composition was confirmed by the electrospray ionization mass spectrometry (ESI-MS), multinuclear NMR, X-ray photoelectron spectroscopy (XPS), UV/Vis, and EDS for the Ag:S atomic ratio. Furthermore, DFT calculations afford to provide a bonding analysis and a rationalization of the stability of **1**.

The single-crystal structure revealed that **1** crystallizes in the monoclinic space group $P2_1/n$ and comprises a monocationic cluster $[Ag_{21}(S_2P(O\textit{i}Pr)_2)_{12}]^+$ along with a $[PF_6]^-$ coun-

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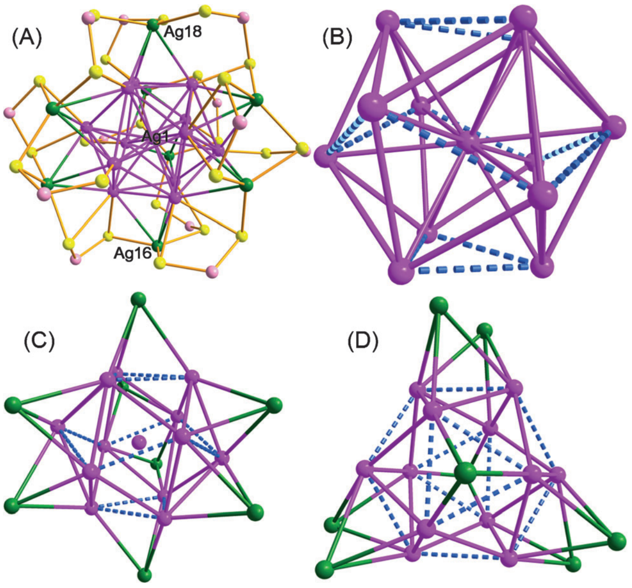

Figure 1. A) Total structure of the cationic $[Ag_{21}\{S_2P(OiPr)_2\}_{12}]^+$ cluster in **1** with isopropoxy groups omitted for clarity. B) A centered icosahedron Ag_{13} (crimson spheres) with view of an Ag_6 corrugated plane (chair) in between a top Ag_3 face and a bottom face in an eclipsed form, which is denoted by dashed edges in blue. C) The Ag_{21} core consisting of a centered icosahedron Ag_{13} and eight capping Ag atoms (green) with a side views along the C_3 axis. D) A top view of Ag_{21} core, where two capping Ag atoms lie on the C_3 axis and six capping Ag atoms are around C_3 in the formation of a three-fold propeller. Ag crimson and green, S yellow, P pink.

terion.[21] As shown in Figure 1 A, the cluster has an Ag_{21} metal core stabilized by 12 dtp ligands with an approximate C_3 axis, which passes through the center of two eclipsed (opposite) triangular faces of Ag_{12} icosahedron and contains an encapsulated Ag1 atom. Alternatively the Ag_{13} centered icosahedron can be depicted as the composition of an Ag_6 corrugated plane (chair) sandwiched between two eclipsed Ag_3 faces (Figure 1 B). It can be seen that eight out of twenty Ag_3 faces of the icosahedron are fully capped by Ag atoms to form an Ag_{21} cage. Two of them (Ag16 and Ag18) lie on the pseudo-C_3 axis and the remaining six locate around the C_3 axis in three groups alongside of alternative edges of an Ag_6 corrugated plane (Figure 1 C). Thus, 6 of the 8 (μ_3-Ag) atoms can be divided into two groups related by approximate C_3 symmetry in such a way that they constitute two almost coplanar triangles in a close-to-eclipsed position (staggering angle: 16.5°) in a three-fold propeller-like shape (Figure 1 D). Thus, the ideal symmetry of the Ag_{21} core is D_3.

Within the centered icosahedron Ag_{13},[17] the radial Ag–Ag distances (2.754–2.816 Å) are smaller compared to peripheral Ag–Ag distances (2.842–2.998 Å). The peripheral Ag–Ag distances are reasonably larger than the Ag–Ag distances (2.813–2.843 Å) of the empty icosahedron Ag_{12} in $[Ag_{44}(p\text{-MBA})_{30}]^{4-}$,[8] which is due to the presence of the central Ag atom in the icosahedron of **1** that constitutes the first example in silver nanocluster chemistry. The Ag–Ag distances (2.846–3.168 Å) of the eight capping (μ_3-Ag) atoms in **1** are comparable with the distances (2.813–2.868 Å) for capping silver atoms at the every triangle of the empty icosahedron in Ag_{44}. All Ag–Ag distances in **1** are significantly shorter than the sum of the van der Walls radii for silver (3.40 Å).[22] The XPS result of **1** shows the existence of both Ag^0 and Ag^I. The Ag $3d_{5/2}$ XPS peak can be resolved into two peaks at binding energies of 368.28 eV and 368.68 eV (Supporting Information, Figure S1), respectively, corresponding to Ag^I and Ag^0 in the cluster.[12c] Further, EDS results of **1** showed Ag and S atomic ratio to be 46.67:53.33 (calc 46.66:53.33; Supporting Information, Figure S2, Table S1). The UV/Vis spectrum of $[Ag_{21}(S_2P(OiPr)_2)_{12}]^{1+}$ cluster in solutions exhibit broad multiband optical absorption that displays five apparent peaks (at 235, 260, 381, 425, and 482) and one shoulder peak at 540 nm (Supporting Information, Figure S3).

The entire metallic Ag_{21} core of **1** is wrapped by twelve dtp ligands in three spherical rows following the ratio of 3:6:3 around the pseudo-C_3 axis. These ligands have either trimetallic tetraconnectivity (η^3: μ_2, μ_2) or trimetallic triconnectivity (η^3: μ_2, μ_1) with one Ag_{ico} and two Ag_{cap} atoms. The ligands in top and bottom rows shows coordination mode of (η^3: μ_2, μ_2) and (η^3: μ_2, μ_1).[23] Whereas in the middle row both types of coordination also exist alternatively within the six ligands and accordingly they can be divided into two groups (3 + 3). Thus, cluster **1** has four types of dtp ligands within three spherical rows in a ratio of 3:(3 + 3):3 owing to their distinct environments. The Ag_{ico}–S distances (avg. 2.670 Å) are longer than Ag_{cap}–S (avg. 2.51 Å) and the S···S bite distances (avg. 3.401(5)) Å. The average of Ag–S distances in the Ag_{44} cluster was also found 2.51 and 2.54 Å.[8] However, distances in **1** are comparable to those Ag_v–S (avg. 2.625(3) Å), Ag_{cap}–S (avg. 2.525(3) Å), and S···S 3.471(4) Å in dtp-stabilized $[Ag_8(H)(dtp)_6]^+$.[14b] With respect to metal to ligand coordination, the 8 capping silver atoms are all in the near-planar AgS_3 coordination mode. Within the Ag_{12} icosahedron, the metal atoms constituting the top and bottom triangular faces exhibit AgS coordination (Ag–S avg. 2.566(5) Å) together with a short non-bonding Ag···S contact (avg. 3.128(6) Å) and AgS_2 (avg. 2.801(6) Å). The six remaining Ag atoms are alternatively in AgS and AgS_2 coordination mode, accordingly with the existence of the pseudo-C_3 axis. Each of the latter atoms exhibit one short and one long Ag–S bond (avg. 2.680(4) Å and 2.829(5) Å, respectively). The existence of these two different coordination modes renders different the top and bottom halves of the cluster, thus lowering the ideal D_3 symmetry of the Ag_{21} core to C_3 in the whole cluster **1**, presumably because of geometrical constraints. Consistent with the X-ray results, the variable-temperature (VT) ^{31}P NMR spectra of **1** rationalize the presence of four types of resonance at 97.3, 98.9, 101.6, 102.6 ppm in a ratio of 3:3:3:3 at −20 °C by splitting of a broad resonance centered at $\delta = 99.4$ ppm at 22 °C (Supporting Information, Figure S4). A septet resonance at −143.0 ppm was also detected for the $[PF_6]^-$ counterion. Additionally, the (^1H,^2H) NMR study of the corresponding compound **1** synthesized by using either $[BH_4]^-$ or $[BD_4]^-$ does not depict any hydride or deuteride resonance (Supporting Information, Figure S5), thus precluding the possibility of hydride presence.

Both the cluster composition and the charge were confirmed by electrospray ionization mass spectrometry

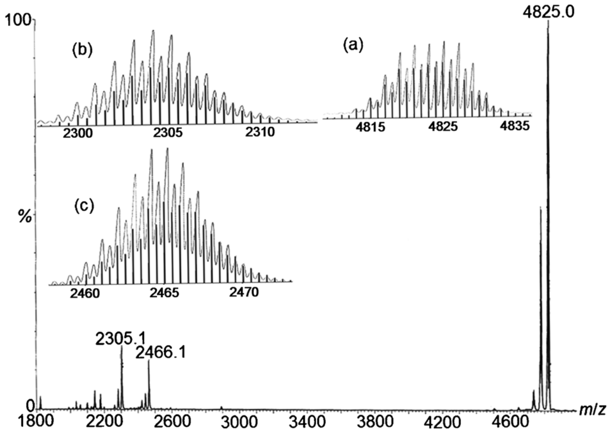

Figure 2. ESI-MS spectrum of **1**. The insets (a), (b), and (c) show experimental (top) and theoretical one (bottom) for the species $[Ag_{21}(S_2P(OiPr)_2)_{12}]^{1+}$, $[Ag_{21}(S_2P(OiPr)_2)_{11}]^{2+}$, and $[Ag_{22}(S_2P(OiPr)_2)_{12}]^{2+}$, respectively.

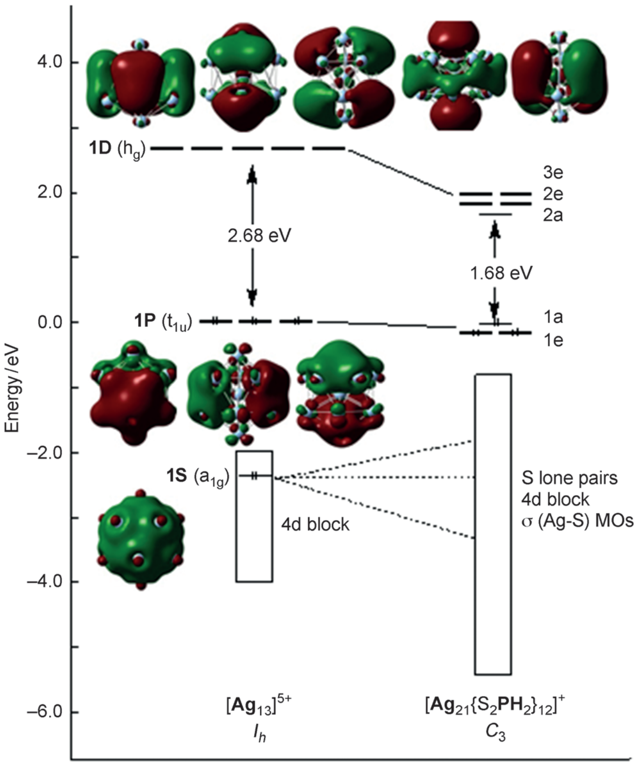

Figure 3. MO diagrams of $[Ag_{13}]^{5+}$ and $[Ag_{21}(S_2PH_2)_{12}]^+$. The MO plots correspond to the Jellium-type orbitals of $[Ag_{13}]^{5+}$. The HOMO energies have been arbitrarily set to zero.

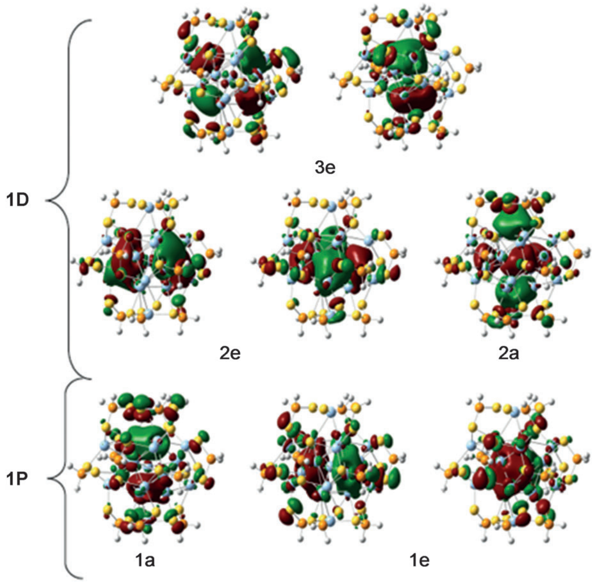

Figure 4. The frontier Jellium orbitals of $[Ag_{21}(S_2PH_2)_{12}]^+$.

(ESI-MS) analysis. ESI-MS (positive mode) revealed prominent peak at $m/z = 4825.0$ (Figure 2), corresponding to the formula of $[Ag_{21}\{S_2P(OiPr)_2\}_{12}]^+$ (calcd = 4823.2). Also observed are two less prominent peaks at $m/z = 2305.1$ and 2466.1 of dicationic species $[Ag_{21}\{S_2P(OiPr)_2\}_{11}]^{2+}$ (calcd = 2305.1) and $[Ag_{22}(S_2P(OiPr)_2)_{11}]^{2+}$ (calcd = 2466.05), respectively. The observed isotopic patterns of $[Ag_{21}\{S_2P(OiPr)_2\}_{12}]^+$, $[Ag_{21}\{S_2P(OiPr)_2\}_{11}]^{2+}$, and $[Ag_{22}\{S_2P(OiPr)_2\}_{12}]^{2+}$ are in excellent agreement with the simulated ones as shown in Figure 2 (insets a, b, and c). Additionally, the as-synthesized compound **1**, by using $[BD_4]^-$ instead of $[BH_4]^-$, shows an almost identical ESI-MS spectrum (Supporting Information, Figure S6), so the possibility of hydride presence in **1** can be ruled out, confirming the (^1H,^2H) NMR results (see above).

Charge balance with the monoanionic ligands implies a +13 formal charge on the Ag_{21} core of **1**, that is, a mixed-valent situation with 8 delocalized metal valence electrons. This electron number is consistent with the superatom concept and corresponds to the closed-shell $1S^2 1P^6$ configuration of the spherical Jellium model.[11] From what is known from other superatom-type clusters,[8,9,11b–c] it can be guessed that the 8 metal electrons are located on the $[Ag_{13}]^{5+}$ spherical cluster core, whereas the 8 capping silver atoms are in their +1 oxidation state and form with the ligands a protecting $[Ag_8\{S_2P(OiPr)_2\}_{12}]^{4-}$ cluster ligand shell. This is confirmed by DFT calculations[24] on the $[Ag_{13}]^{5+}$ and $[Ag_{21}(S_2PH_2)_{12}]^+$ models, the MO diagram of which are shown in Figure 3. Their optimized geometries were found to be of I_h and C_3 symmetry, respectively. Despite their mixed valent nature but consistently with the Jellium shell-closure, their computed HOMO–LUMO gaps are large (2.86 eV and 1.68 eV, respectively). The frontier Jellium-type orbitals of $[Ag_{13}]^{5+}$ and $[Ag_{21}(S_2PH_2)_{12}]^+$ are plotted in Figure 3 and Figure 4, respectively, except for the 1S level of $[Ag_{21}(S_2PH_2)_{12}]^+$, which affords substantial mixing with several occupied MOs of the same symmetry. They exhibit similar shapes and compositions (mainly Ag 5s).

The optimized Ag–Ag distances of $[Ag_{13}]^{5+}$ are 2.983 Å (Ag_{center}–Ag_{ico}) and 3.136 Å (Ag_{ico}–Ag_{ico}). They compare well with the corresponding average values of the Ag_{13} core of $[Ag_{21}(S_2PH_2)_{12}]^+$ (2.881 Å and 3.029 Å, respectively). These latter values are also consistent with their experimental counterparts in **1** (2.779 Å and 2.922 Å, respectively). As may be expected from simple Hückel theory, the central atom in $[Ag_{13}]^{5+}$ is more negatively charged than the peripheral ones (natural atomic charges: −0.86 vs. +0.49). The corresponding values in $[\mathrm{Ag}_{21}(\mathrm{S}_2\mathrm{PH}_2)_{12}]^+$ are −0.44 and +0.23, whereas the average charge of the capping silver(I) atoms is +0.62. The ($\mathrm{Ag}_{\mathrm{center}}$–$\mathrm{Ag}_{\mathrm{ico}}$ and $\mathrm{Ag}_{\mathrm{ico}}$–$\mathrm{Ag}_{\mathrm{ico}}$) Wiberg indices in $[\mathrm{Ag}_{13}]^{5+}$ and $[\mathrm{Ag}_{21}(\mathrm{S}_2\mathrm{PH}_2)_{12}]^+$ are comparable and consistent with significant covalent bonding (0.192/0.089 and 0.134/0.081 Å, respectively). On the other hand, the $\mathrm{Ag}_{\mathrm{cap}}$–$\mathrm{Ag}_{\mathrm{ico}}$ values in $[\mathrm{Ag}_{21}(\mathrm{S}_2\mathrm{PH}_2)_{12}]^+$ (avg. +0.035) correspond to what is usually found for $\mathrm{d}^{10}\cdots\mathrm{d}^{10}$ bonding interactions.

In summary, we have presented the one-pot synthesis and crystal structure determination of a novel $[\mathrm{Ag}_{21}(\mathrm{S}_2\mathrm{P}(\mathrm{O}i\mathrm{Pr})_2)_{12}]^+$ nanoparticle protected by dithiophosphate ligands, which features an unprecedented silver-centered icosahedron Ag_{13} with additional eight capping silver atoms to constitute an Ag_{21} cage. Multinuclear NMR study and ESI-mass spectrometry support the structure and formula. DFT calculations indicate that the stability of this silver nanocluster can be rationalized as that of an 8-electron $[\mathrm{Ag}_{13}]^{5+}$ superatom (with $1\mathrm{S}^2 1\mathrm{P}^6$ Jellium closed-shell configuration) protected by a $[\mathrm{Ag}_8\{\mathrm{S}_2\mathrm{P}(\mathrm{O}i\mathrm{Pr})_2\}_{12}]^{4-}$ external shell.[25] It should be noted that applying the same method of synthesis with copper(I) salts, only copper(I) hydride clusters have been isolated so far,[16] whereas with silver(I) salts the title mixed valence compound is one of the large silver clusters isolated to date. Incidentally the Ag_{21} nanocluster obtained also provides a key intermediate on the way to silver nanoparticles from those hydride-containing precursors.[14d]

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