[Cu$_{81}$(PhS)$_{46}$(BuNH$_2$)$_{10}$(H)$_{32}$]$^{3+}$ Reveals the Coexistence of Large Planar Cores and Hemispherical Shells in High-Nuclearity Copper Nanoclusters

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ABSTRACT: Copper-based nanomaterials have attracted tremendous interest due to their unique properties in the fields of photoluminescence and catalysis. As a result, studies on the correlation between their molecular structure and their properties are of great importance. Copper nanoclusters are a new class of nanomaterials that can provide an atomic-level view of the crystal structure of copper nanoparticles. Herein, a high-nuclearity copper nanocluster with 81 copper atoms, formulated as [Cu$_{81}$(PhS)$_{46}$(BuNH$_2$)$_{10}$(H)$_{32}$]$^{3+}$ (Cu$_{81}$), was successfully synthesized and fully studied by X-ray crystallography, X-ray photoelectron spectroscopy, hydrogen evolution experiments, electrospray ionization mass spectrometry, nuclear magnetic resonance spectroscopy, and density functional theory calculations. Cu$_{81}$ exhibits extraordinary structural characteristics, including (i) three types of novel epitaxial surface-protecting motifs; (ii) an unusual planar Cu$_{17}$ core; (iii) a hemispherical shell, comprised of a curved surface layer and a planar surface layer; and (iv) two distinct, self-organized arrangements of protective ligands on the curved and planar surfaces. The present study sheds light on structurally unexplored copper nanomaterials and paves the way for the synthesis of high-nuclearity copper nanoclusters.

INTRODUCTION

The synthesis of atomically precise ultrasmall metal nanoparticles (1–3 nm) is a major achievement in nanoscience. Usually, referred to as nanoclusters — to differentiate them from conventional nanoparticles — these nanomaterials have well-defined molecular structures determined by X-ray crystallography, thus providing a direct path for correlating the material’s structure to its chemical and physical properties at the atomic level and the necessary basis for predicting properties of compositionally related materials that are not amenable to full-structural characterization methods. Among nanoclusters, coinage-metal (e.g., copper, silver, gold, and their alloys) composites have attracted immense interest not only for their fascinating molecular structures but also due to their potential applications in imaging and catalysis. Recent reports have demonstrated that the geometric construction of a nanocluster’s core can govern the structure, size, and optical properties of the nanoparticles, while the shell configuration, including the shape, surface area, and self-organizational behaviors of the protecting ligands, plays a critical role in the particle’s stability, solubility, aggregation state, catalytic activity, and photoluminescence properties.

In silver and gold, where significant advances have been achieved, the pursuit of high-nuclearity nanoclusters (e.g., Ag$_{141}$, Ag$_{146}$, Ag$_{206}$, Ag$_{215}$, Ag$_{254}$, etc.; and Au$_{32}$, Au$_{133}$, Au$_{144}$, Au$_{236}$, Au$_{362}$, etc.) has provided new insights into the transition from the nonmetallic to the metallic state and the mechanisms of formation, growth, and evolution of silver and gold nanoparticles. In contrast, the development of
Copper is vulnerable to air oxidization due to its wide range of accessible oxidation states (Cu⁰, Cu¹, Cu², and Cu³) which has hampered progress in the synthesis of copper nanoclusters. To date, only a handful of high-nuclearity copper nanoclusters have been reported, and the largest known cluster contains 61 copper atoms with a quasi-I₃₀ Cu₉₀ core. The lack of structural information on copper nanoclusters significantly limits our fundamental understanding of the structure-dependent properties and the development of applications of copper nanomaterials. Hence, expanding the limited library of copper nanoclusters, especially those with high nuclearity, is of utmost importance.

Herein, we report a one-pot direct reduction strategy to synthesize a high-nuclearity copper nanocluster. The cluster’s atomic structure and composition were determined through single crystal X-ray diffraction (SC-XRD) and electrospray ionization mass spectrometry (ESI-MS), supported by X-ray photoelectron spectroscopy (XPS), hydrogen evolution experiments, and nuclear magnetic resonance (NMR) spectroscopy. The synthesized copper nanocluster, [Cu₈₁(PhS)₈₁(BuNH₂)₁₀(H)₂]⁺ (where PhS is benzenethiol and BuNH₂ is tert-butylamine), contains 81 copper atoms, denoted as Cu₈₁. This cluster defies conventional expectations for high-nuclearity nanoclusters, which typically contain a polyhedron-based core (e.g., tetrahedron, octahedron, decahedron, dodecahedron, icosahedron, cuboctahedron, and the converted/derived structures) surrounded by a symmetric conformal shell. In contrast, Cu₈₁ exhibits an unprecedented planar core containing 17 copper atoms. The planar core is enclosed by a hemispherical shell, which is comprised of a curved surface layer and a planar surface layer, bound together by three types of novel epitaxial surface-protecting motifs. These geometric features profoundly affect the arrangement of the aromatic ligands on the surface of the cluster. The aromatic ligands on these two types of surface layers self-organized into disparate patterns, where weak intermolecular interactions, such as π–π stacking and C–H⋯π interactions, play a crucial role in directing and stabilizing the surface patterns. Cu₈₁ reveals a new structural archetype for metal nanoclusters – beyond the canonical series of polyhedral-based core configurations – and the consequences of this architecture on surface ligand self-organizational behaviors.

RESULTS AND DISCUSSION

Synthesis and crystallization. The Cu₈₁ nanocluster was synthesized by a one-pot direct reduction strategy. In brief, the reaction of [Cu(CH₃CN)₆]BF₄ and PhSH in acetonitrile with a mild reducing agent, borane tert-butylamine complex (BuNH₂•BH₃), immediately resulted in a crimson solution at room temperature (23°C). After stirring for ten minutes, the solvent was concentrated by rotary evaporation to give a red residue. Subsequently, this residue was dissolved in a mixed solvent of chloroform/hexane and kept in a sealed glass vial, yielding red rhombohedral crystals in six days (Figure 1a) (details of the method are presented in the Experimental Section). The whole synthesis and crystallization procedure was carried out under ambient conditions.

Structure analysis of Cu₈₁. An as-obtained crystal was structurally characterized by SC-XRD. The structure of the Cu₈₁ nanocluster is shown in Figure 1. Analysis of the crystallographic data revealed that Cu₈₁ contains 81 copper atoms, 46 PhS⁻ ligands, and 10 auxiliary ligands (BuNH₂). Morphologically, from the top view (Figure 1b), Cu₈₁ displays an irregular shape with a distance of 2.8 nm between the two farthest benzene ring carbon atoms, and from the side view (Figure 1c), it resembles a hemispherical dome (~1.5 nm in height) with one curved surface and one planar surface. The Cu₈₁ nanoclusters packed into a monoclinic lattice, C2/c space group, with a packing density of ~65% (Figure S1 and Table S1). Each Cu₈₁ nanocluster in the same stacking layer (001) is arranged uniformly with identical orientations, yet the orientation of the nanoclusters is opposite that in the adjacent stacking layer (Figure S1). The stacking layers are perpendicular to the [001] direction.

Figure 1. (a) Optical microscopy image of Cu₈₁ crystals. Top (b) and side (c) views of Cu₈₁. Brown (shell)/green (core): Cu; yellow: S; blue: N; gray: C. The carbon tails are shown in wireframe mode, and all hydrogen atoms have been omitted for clarity.

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The architecture of the Cu$_{161}$ cluster can be divided into two major components (Figure 2) in accordance with conventional structural decomposition strategies: the main body and the epitaxial surface-protecting motifs. As shown in Figure 2, six epitaxial motifs exhibit three different types of staple-like configurations: a linear monomeric motif, a bent monomeric motif, and a cyclic trimeric motif. Each type has two units bridged to the main body about the crystallographic inversion center. Although oligomeric staple-like motifs are quite common in silver and gold clusters, they are rarely observed in copper clusters. For the linear monomeric motif, the Cu atom is bonded to two PhS– ligands with an S–Cu–S angle of approximately 180° (Figure S2a). The PhS– ligand coordinates to the Cu atoms in the staple and main body with Cu–S bond lengths ranging from 2.166 to 2.204 Å, and the aromatic rings in these two ligands lie on the same side. In the bent monomeric motif, owing to the insertion of a bulky BuNH$_2$ ligand, the aromatic rings point in different directions with an S–Cu–S angle of 107°, and the PhS– ligands take the μ$_3$-$η^1$, $η^1$, $η^1$ coordination mode with Cu–S distances of 2.193–2.352 Å (Figure S2b). Interestingly, the cyclic trimeric motif Cu$_2$(PhS)$_3$ adopts a distorted chair conformation, in which all the internal angles are different; the average S–Cu–S angle is 109°, and the average Cu–S–Cu angle is 85° (Figure S2c). The PhS– ligands take the μ$_2$-$η^3$, $η^1$, $η^1$, coordinate mode, and each BuNH$_2$ bridges one Cu atom by Cu–N bond (Figure S2c). This type of cyclic trimeric motif has not been previously observed in coinage-metal nanoclusters.²

![Figure 2](image)

**Figure 2.** The total skeleton of Cu$_{161}$ is shown in the ball-and-stick model, and it is composed of the main body and epitaxial surface-protecting motifs. There are three different types of staple-like epitaxial motifs on the surface of the Cu$_{161}$ nanocluster. Carbons are drawn in the stick model. Brown (shell)/green (core): Cu; yellow: S; blue: N; gray: C.

As shown in Figure 3, the main body, which is composed of 71 Cu atoms, 32 PhS– ligands and two BuNH$_2$ ligands, can be separated into three layers: an upper layer, a middle layer, and a bottom layer. For a more detailed dissection of the main body structure, we start with the skeleton constructed by Cu–S bonds and Cu–Cu cuprophilic interactions (Table S2). It is important to note that cuprophilic interactions, an attractive force between closed-shell d$^{10}$ copper atoms, requires Cu–Cu distances shorter than the orbital interaction radius, are roughly comparable to hydrogen bonds in strength.⁵⁷ Nevertheless, the presence and length of such interactions are both still highly controversial, and we here tentatively define only Cu⋯Cu distances shorter than 2.8 Å (the van der Waals radius of Cu is 1.4 Å) as cuprophilic interactions.

From the side view, the upper layer is in the shape of a “moon bridge” constructed by one curved “bridge deck” and two M-shaped “piers” (Figures 3c, d, and S3). The “pier” consists of two PhS– ligands and three Cu atoms (Figures S4a). These three Cu atoms are strung together through cuprophilic interactions in the range of 2.573–2.624 Å (Figures S4b). The PhS– ligands adopt the μ$_2$-$η^1$, $η^1$, $η^1$ coordination mode with Cu–S distances being 2.236–2.355 Å (Figure S5). The “bridge deck” comprises 16 PhS– ligands and 24 Cu atoms, in which these ligands are arranged in three distinguishable lines (5+6+5) connected by Cu–S bonds (Figures S4c and d). Four of the ligands adopt the μ$_2$-$η^1$, $η^1$, $η^1$, $η^1$ mode with Cu–S distances being 2.369–2.480 Å, and the remaining 12 PhS– ligands take the μ$_2$-$η^1$, $η^1$, $η^1$ mode with Cu–S distances of 2.197–2.480 Å (Figure S6). In addition to the abundant Cu–S covalent bonds, five cuprophilic interactions of 2.610–2.785 Å were observed in the “bridge deck” (Figure 6a). Intriguingly, the middle layer is a slightly curved plane consisting of 17 Cu atoms, which is fully encapsulated within the skeleton of the main body (Figures 3e, f, and S7). Alternatively, the middle layer can also be viewed as a planar core built by cuprophilic interactions of 2.544–2.792 Å that is enclosed in a hemispherical shell comprising a curved surface layer, a planar surface layer, and six epitaxial surface-protecting motifs. (Figures 4 and S7). In this planar Cu$_{17}$ core, 20 triangles are formed with copper atoms as the vertices and Cu⋯Cu interactions as the edges (Figure 4). The Cu$_{17}$ core lies in the middle of the shell, which is supported by cuprophilic interactions and Cu–S bonds (Figure S8). The Cu⋯Cu and Cu–S distances are in the range of 2.440–2.797 and 2.298–2.319 Å, respectively. Despite numerous reported monolayer-protected Ag and Au nanoclusters with core-shell structures,²⁻³ the core seen in Cu$_{161}$ is unique and has not been observed among copper nanoclusters or analogous metal nanoclusters, and this is a new structural archetype for metal nanoclusters beyond the series of canonical polyhedron-based core configurations.

![Figure 3](image)

**Figure 3.** Ball-and-stick models of the main body showing the top (a) and side (b) views; (c), (d) the top and side views of the upper layer; (e), (f) the top and side views of the middle layer; (g), (h) the
top and side views of the bottom layer. Brown (shell)/green (core/middle layer): Cu; yellow: S.

The planar bottom layer consists of 24 Cu atoms and 12 PhS–ligands. A planar layer of this size is rare in X-ray structures of coinage-metal nanoclusters. On the bottom layer, 12 PhS–ligands adopt two types of ligation modes: 8 take the μ₄-η¹, η¹, η¹, η³ mode and 4 adopt the μ₃-η¹, η¹, η¹ mode (Figures 3g, h, and S9). All 24 copper atoms are connected by abundant cuprophilic interactions. The Cu–Cu distances fall in the range of 2.443–2.650 Å, indicating the important role of cuprophilic interactions in stabilizing the bottom layer (Figure S10).

In contrast to the surface ligand coverage (i.e., the ratio of the number of thiolates to surface metal atoms) of 67% in the curved upper layer, the planar bottom layer shows a much lower value of 50%, which is even lower than that of the nanocluster protected by bulky ligands, implying that the planar bottom layer has a higher surface reactivity. So, if nanoclusters favor higher surface ligand coverage (i.e., lower surface reactivity), then our case seems to provide a plausible explanation for why most reported high-nuclearity nanoclusters are nearly spherical. Additionally, the previously reported monolayer-protected nanoclusters possess only curved or only planar surface layers, and Cu₃₁ is the first example that has both types of surface layers, which makes it a very interesting model for studying the self-organizational behaviors of surface-protecting ligands.

![Figure 4](image)

Figure 4. The core-shell structure of Cu₃₁. All C, N, and H atoms were omitted for clarity. Brown (shell)/green (core/middle layer): Cu; yellow: S.

The study of the patterning laws of surface-protecting ligands in nanoclusters is attracting increasing attention because it is not only helping to determine the driving forces and rules that direct the self-organization of surface ligands but also important for understanding the correlations between structure and stability. In this nanocluster, the patterns of aromatic rings on the curved upper and planar bottom layers are significantly different (Figure 5). As shown in the space-filling model of the surface aromatic rings (Figure 5a), the “bridge deck” of the upper layer was completely covered by PhS–ligands. The phenyl rings on the “bridge deck” exhibit a herringbone-like pattern with an average dihedral angle and centroid–centroid distance (between neighboring molecules) of 60° and 4.92 Å, respectively (Figures 5b and c). These PhS–ligands are further connected together by an intermolecular C–H–π interaction network, in which the ortho-C atoms of the phenyl rings interact with the ortho-C atoms of the facing π-planes with H–π distances in the range of 2.65–2.97 Å and H-C-O-C (θ) angles ranging from 9.99° to 41.94° (Figure 5c). The herringbone-like arrangement was also observed in a high-nuclearity Au cluster, in which the herringbone pattern was constructed via a combination of intercluster and intracluster ligand–ligand interactions, rather than self-assembly on a single surface layer of the cluster. Although C–H–π interactions are weak intermolecular forces, the intracluster C–H–π interaction network is quite important to the self-organization of the aromatic ligands on the nanoclusters, as it can generate an energy barrier and stabilize the surface pattern.

![Figure 5](image)

Figure 5. (a) The arrangement of aromatic rings on the “bridge deck” of the upper layer displayed in the space-filling model (based on the van der Waals radius of each atom). (b) A schematic of the aromatic rings on the “bridge deck” of the upper layer showing a herringbone-like pattern. (c) The C–H–π interaction network (orange dashed lines) in the upper layer. The H-C-O-C angle is defined as θ, and θ should be smaller than 60°. Brown: Cu; yellow: S; light turquoise: H. (d) The arrangement of aromatic rings on the bottom layer displayed in the space-filling model. (e) The C–H–π (orange dashed lines) and π–π (yellow dashed lines) interactions on the bottom layer. Brown: Cu; yellow: S; blue/lavender: C; light turquoise: H.

In contrast to the concise esthetic pattern of the aromatic rings on the upper layer, the patterns on the bottom layer are more complex. As shown in Figure 5d, the bottom surface layer is compactly paved with 12 phenyl rings, which can be divided into three groups (A, B and C). Groups A and C have the same arrangement, while their directions are opposite. The four
benzene rings in group B are in a parallel-displaced configuration with an average centroid–centroid distance and displacement angle of 3.80 Å and 21°, respectively, which indicate the presence of π···π interactions between adjacent aromatic rings (Figure S11). These three groups are further connected by C–H···π interactions with an average H···π distance of 2.80 Å, forming an intracluster ligand–ligand interaction network. (Figure 5e).

The above observations and analysis demonstrate that the self-organizational behaviors of the protecting ligands on the nanocluster surface are not only affected by the ligand structure and the area and shape of the surface layer but also influenced by weak intermolecular interactions, such as π···π stacking and C–H···π interactions. In addition, due to the basic requirement of structural stability, regardless of the shape of the surface layer, the protecting ligands should cover as many surfaces as possible, and there seems to be a balance between steric hindrance and coverage.

To further study the intermolecular interactions between phenyl rings within both the upper and bottom layers, we calculated the charge transfer integrals ($I_{CT}$) between the neighboring benzene rings based on a dimer model using DFT, which can quantify the intermolecular electronic couplings for hole/electron transfer between nearest-neighbor phenyl rings (the higher the $I_{CT}$ value, the higher the charge carrier mobility is). As shown in Figure S12, the average $I_{CT}$ values of holes/electrons (25.3/107.8 meV) for the bottom layer are almost 2.5 times larger than those for the upper layer (10.8/42.8 meV) due to the stronger π-orbital overlap between the phenyl rings. We also evaluated the electronic interactions between the nearest-neighbor clusters. The average $I_{CT}$ values for holes/electrons (4.1/5.8 meV) suggest the presence of intercluster charge transfer originating from electronic coupling between phenyl rings from neighboring clusters (Figure S13). Our DFT results suggest that (i) the strength of electronic interactions among surface ligands is mainly determined by the surface pattern and (ii) the surface ligands could facilitate efficient charge transport between the cluster units in the solid crystal.

**Hydride and Composition Analysis.** The presence of hydrides in a copper nanocluster synthesized by a reaction with excess borohydride is rather common and seems to be due to the electronegativity of copper. Additionally, the hydrides play an important role in constructing and stabilizing the geometric structure of the copper nanoclusters. However, it is very difficult to identify the hydrides in high-nuclearity copper nanoclusters via a Fourier difference map because the scattering contribution of hydride to X-ray is much lower than that of its closely bound copper atom (Cu–H: 1.5–1.9 Å). Neutron diffraction is a well-known alternative to unequivocally determine the location of hydrides. Unfortunately, we were unable to crystallize Cu$_{81}$ into a crystal sufficiently large for neutron diffraction measurements.

**Figure 6.** (a) ESI-MS spectrum of Cu$_{81}$ in positive mode. Inset: experimental isotope pattern (black trace) of the peak k are in perfect agreement with its simulated isotope pattern (red trace). (b) Expansion of the mass spectrum showing the experimental (black trace) and simulated (red trace) isotope patterns for each labeled species.

To ascertain the total composition, especially the hydride content, the charge state of cluster, and the counterions present, we studied the CHCl$_3$ solution of Cu$_{81}$ with ESI-MS. ESI-MS is a very powerful and reliable tool for the analysis of composition and structure and even for exploring the reaction mechanisms of nanoclusters due to its “soft” ionization nature. Here, ESI-MS was performed using a Bruker MicroTOF-II mass spectrometer. A positive ion ESI-MS spectrum of Cu$_{81}$ is presented in Figure 6, where one prominent signal with a charge state of +3 was observed in the mass range of m/z 2000–10000, and that signal consisted of a series of peaks (labeled from a to t). The most abundant peak centered at m/z = 3400.30 (k) can be assigned to [Cu$_{81}$ (PhS)$_{46}$ (H)$_{26}$]$^{+}$ (Calc. m/z = 3400.34), which is derived from the loss of the BuNH$_2$ molecules from the parent cluster. After expanding the m/z 3000–4000 region (Figure 6b), peak k was found to be in the middle of these peaks. The Δm/z between k and m is 57.6, which is the same as the Δm/z between j and l, corresponding to a mass difference equivalent to one PhSCu. The other labeled species in Figure 6b were also identified and are listed in Table S3. The number of hydrides was found to be constant at 32 in all the species. Notably, those peaks are regularly distributed on both sides of k with the same composition change, suggesting the presence of a dynamic coordination-disassociation equilibrium of the protecting ligands on Cu$_{81}$ in solution. The same phenomenon has been observed in previously reported high-nuclearity nanoclusters.

To further verify the presence of hydrides, ESI-MS of the corresponding deuteride analogue, Cu$_{81D}$, was performed using fresh crystals, which were synthesized following the same procedure used to prepare Cu$_{81}$ but with a deuterated analogue of $^{13}$BuNH$_2$BH$_3$. $^{13}$BuNH$_2$BD$_3$ instead of $^{13}$BuNH$_2$BH$_3$. The mass spectrum of Cu$_{81D}$ features a prominent signal in the mass range of m/z 3000–4000 similar to that of Cu$_{81}$, and it comprises a series of peaks with a charge state of +3 (Figure
measurements. Inside the semispherical shell by referring to the hydride crystallographic structure, in which 32 hydrides were placed. The initial cluster model was built based on the X-ray performed geometry optimizations by DFT calculations. The obtained: $[\text{Cu}^{+1}]_{\text{32}}$. Finally, the definite molecular formula of the counterions. The number of hydrides and the valence state of the $\text{Cu}$ carries a charge of 3+, which is balanced by three $\text{BF}_4^{-}$.

To determine the positions of the 32 hydrides in the DFT calculations. The initial cluster model was built based on the X-ray crystallographic structure, in which 32 hydrides were placed inside the semispherical shell by referring to the hydride positions in previously reported hydride-containing copper clusters determined through neutron diffraction measurements.

**Figure 7.** (a) Optimized geometry of $\text{Cu}_{\text{32}}$ obtained from DFT calculations (the aromatic rings of –PhS and $\text{BuNH}_2$ are omitted). (b) Top view and (c) side view of the optimized structure (the surface ligands and the $\text{Cu}$ atoms that are not directly bound to hydride are omitted). The hydrides that are within different structural environments. Among them, 18 hydrides are symmetrically distributed in the crescent space between the upper and middle layers of the cluster (Figures 7b, c, and S16). Ten hydrides take the $\mu_4$ coordination mode and the remaining eight have the $\mu_3$ mode. $\mu_4$-H is in a tetrahedral cavity consisting of three $\text{Cu}$ atoms in the middle layer and one $\text{Cu}$ atom in the upper layer (Figures S16b, c). $\mu_3$-H caps a $\text{Cu}_3$ triangle, forming a pyramidal geometry. Obviously, the $\text{Cu}$ atoms in the middle layer are fixed by these interstitial hydrides ($\text{Cu}$–H: 1.668–1.824 Å). Between the middle and bottom layers, a fusiform space is filled by 8 hydrides, four with $\mu_4$ mode and four with $\mu_3$ mode, and the $\text{Cu}$–H distances are in the range of 1.637–1.838 Å (Figures 7c and S16d). The remaining 6 hydrides coprotecting the bottom layer with PhS– ligands adopt a triangular-face-capping coordination mode with the $\text{Cu}$–H distances of 1.686–1.885 Å (Figures S16f and g).

Due to the large size of $\text{Cu}_{\text{32}}$, the optimizations used a strategy in which only the hydrides were allowed to relax at first and then both the $\text{Cu}$ and hydrides were fully relaxed. The optimized structure of $\text{Cu}_{\text{32}}$ is shown in Figure 7a, and it is in agreement with the crystallographic structure (see the comparison of the average bond lengths in Figure 7d). In the optimized structure, the 32 hydrides can be categorized into three groups in a ratio of 18:8:6 according to their different structural environments. Among them, 18 hydrides are symmetrically distributed in the crescent space between the upper and middle layers of the cluster (Figures 7b, c, and S16). Ten hydrides take the $\mu_4$ coordination mode and the remaining eight have the $\mu_3$ mode. $\mu_4$-H is in a tetrahedral cavity consisting of three $\text{Cu}$ atoms in the middle layer and one $\text{Cu}$ atom in the upper layer (Figures S16b, c). $\mu_3$-H caps a $\text{Cu}_3$ triangle, forming a pyramidal geometry. Obviously, the $\text{Cu}$ atoms in the middle layer are fixed by these interstitial hydrides ($\text{Cu}$–H: 1.668–1.824 Å). Between the middle and bottom layers, a fusiform space is filled by 8 hydrides, four with $\mu_4$ mode and four with $\mu_3$ mode, and the $\text{Cu}$–H distances are in the range of 1.637–1.838 Å (Figures 7c and S16d). The remaining 6 hydrides coprotecting the bottom layer with PhS– ligands adopt a triangular-face-capping coordination mode with the $\text{Cu}$–H distances of 1.686–1.885 Å (Figures S16f and g). From an architectural point of view, the arrangement of 32 hydrides in the optimized structure sufficiently indicates that the hydrides play a critical role in constructing and stabilizing this unconventional nanocluster configuration.

XPS was employed to corroborate the chemical composition and chemical state of $\text{Cu}_{\text{32}}$. The XPS survey spectrum of $\text{Cu}_{\text{32}}$ revealed the presence of all the expected elements ($\text{Cu}$, S, C, N and F) (Figure S17a). The high-resolution XPS spectra of $\text{Cu}$ 2p, S 2p, N 1s, F 1s, and C 1s are shown in Figures S17b–f. The detected F 1s signal come from the $\text{BF}_4^{-}$ anion, which acts as the counterion in $\text{Cu}_{\text{32}}$. The high-resolution XPS spectrum of copper shows sharp doublets originating from $\text{Cu}_{2p_{3/2}}$ and $\text{Cu}_{2p_{1/2}}$ at 932.8 and 952.6 eV, respectively (Figure S17b), in good agreement with those of $\text{Cu}(I)$. Moreover, there is no observable satellite signal at approximately 943 eV, demonstrating the absence of $\text{Cu}(II)$ in $\text{Cu}_{\text{32}}$. Moreover, the Cu LMM Auger spectra of $\text{Cu}_{\text{32}}$ and $\text{[Cu(CH}_3\text{CN}_4]}\text{BF}_4$ were also collected and analyzed to elucidate the oxidation states of the copper atoms. As shown in Figure S18, the almost overlapping curves distinctly indicate that all the copper atoms are in the $+1$ state, which is consistent with the conclusion of ESI-MS analysis.

To further demonstrate the existence of hydride in the as-synthesized $\text{Cu}_{\text{32}}$, a hydrogen evolution experiment was carried out using a mass spectrometer equipped with a laboratory-scale fix-bed reactor. The details of the instrumentation and sample preparation are presented in the supporting information. As a comparison, reported hydride-containing cluster $\text{Cu}_{\text{32}}^{16}$ was measured under identical conditions. As shown in Figure S19, substantial release of $\text{H}_2$ was observed when the temperature was increased to approximately 93 °C, which strongly suggests the presence of hydride in $\text{Cu}_{\text{32}}$. In contrast to the sharp liberation of $\text{H}_2$ by $\text{Cu}_{\text{32}}$, $\text{Cu}_{\text{32}}$ exhibits a continuous triple liberating behavior, implying that the hydrides in $\text{Cu}_{\text{32}}$ are in at least three distinct chemical environments. Additionally, the hydrides in $\text{Cu}_{\text{32}}$ are more sensitive to temperature because the $\text{Cu}_{\text{32}}$ crystals start to liberate $\text{H}_2$ at approximately 93 °C, which
is much lower than that of Cu$_{63}$ (142 °C). This kind of hydride-containing copper cluster is of potential value for hydrogen storage applications because it can release H$_2$ under certain external stimuli.\footnote{5}

Furthermore, the high-resolution solid-state 1D $^1$H MAS coupled with 2D $^1$H–$^1$D DQ NMR spectra were acquired to gain the structural and dynamical information of the surface-protecting ligands and hydrides in Cu$_{63}$. The $^1$H MAS NMR spectrum of the as-synthesized sample displays two major overlapping signals covering the range from 12 to $~2$ ppm (Figure S20). The very broad peak without resonance fine structure centered at 6.16 ppm, corresponding to the proton signals of the benzene rings, suggests the strongly restricted rotation of these PhS– ligands, which is a result of intercluster and intracluster ligand–ligand interactions. Another peak centered at 0.75 ppm can be assigned to the –CH$_3$ of BuNH$_2$. The 2D $^1$H–$^1$H DQ spectrum also confirmed the presence of weak intermolecular interactions between adjacent PhS–ligands (Figure S21). However, the hydride signal was not observed in these spectra due to the masking caused by the broad signals of PhS– and BuNH$_2$. We next studied the $^1$H NMR spectra of Cu$_{63}$ in CDC$_3$ at a very low concentration ($0.5$ mM). We suppose that the Cu$_{63}$ clusters are monodispersed and that the intercluster ligand–ligand interactions are negligible in such dilute solutions. As shown in Figure S22, the extremely broad signal ranging from 4.8 to 8.1 ppm corresponds to the protons of the phenyl groups. By comparison of the aromatic signals of the cluster and free PhSH (7.4–7.2 ppm), it is clear that the majority of the peaks corresponding to PhS– ligands are shifted upfield ($<7.2$ ppm) due to the shielded ligand environments caused by C–H···π aromatic interactions, while only a fraction of the peaks exhibit downfield shifts ($>7.4$ ppm) due to the deshielding effect resulting from the π···π aromatic interactions. This finding is in quantitative agreement with the observation of the corresponding intermolecular interactions of PhS–ligands that were noted from the crystallographic structure. While affecting the chemical shift of the ligand, the intermolecular interactions can also restrict the rotation of the phenyl group, consequently leading to the perceived broadening of the peaks stemming from the aromatic signals.\footnote{6} Additionally, the temperature-dependent $^1$H NMR spectra show that the peaks at approximately 5.5 ppm gradually sharpen and shift downfield with increasing temperature (Figure S23), revealing that the rotation of the phenyl groups on the cluster surface is largely restricted in the temperature range of 273–333 K. The above results clearly indicate that the intrinsic arrangement of the surface-protecting ligands of Cu$_{63}$ can be largely preserved in the solution state, which may be due to the stabilizing effect of the intracluster ligand–ligand interaction networks.

In the $^1$H NMR spectrum of Cu$_{63}$, the broad peak centered at $~2.5$ ppm and partially overlapping with the ‘BuNH$_2$ signal can be assigned to the hydrides. This peak is absent in the $^1$H NMR spectrum of Cu$_{63}$ip (Figure S24), further confirming its attribution to the hydrides. Additionally, we collected the temperature-dependent $^1$H NMR spectra of Cu$_{63}$ from 213 to 298 K. As shown in Figure S25, the extremely broad peak ranging from 4.5 to $0.8$ ppm, corresponding to the deuteride hydrides, comprises a series of subpeaks. However, this hydride signal did not split into well-resolved and integrable peaks even when the temperature was lowered to 213 K, which is due to the low symmetry and anisotropic structure of the Cu$_{63}$ cluster as well as the multiple chemical environments of the hydrides. We also carried out theoretical calculations to determine the $^1$H NMR chemical shifts of all the protons on the Cu$_{63}$ nanoprecursor as well as the hydrides. The experimental and calculated $^1$H NMR chemical shifts are given in Table S4. The correlation plot is linear with a correlation coefficient of 0.99, suggesting good agreement between the experimental and calculated chemical shifts (Figure S26).

The steady-state UV-Vis spectrum of the Cu$_{63}$ nanoprecursor in CHCl$_3$ shows a monotonic decrease in absorbance (Figure S27a). Its optical band gap is estimated to be 1.74 eV by extrapolation of the absorbance to the baseline (Figure S27b). This extrapolated band gap is larger than the calculated energy gap of 0.91 eV (Figure S28) due to the well-known underestimated band gap values typically obtained by the GGA/PBE level of calculations. The electronic charge densities of the frontier orbitals are shown in Figure S28. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are both primarily composed of Cu and S and are delocalized over the planar core, suggesting that the HOMO→LUMO transition occurs in the core. The atomic charges of all copper atoms in Cu$_{63}$ fall into the 0.44–0.85 range, corroborating the assigned Cu(I) oxidation state. The average atomic charge of the hydrides is $-0.32$.

**CONCLUSION**

We successfully synthesized and structurally characterized a high-nuclearity core-shell copper nanoprecursor, [Cu$_{63}$((PhS)$_{50}$BuNH)$_{20}$(H)$_{30}$]$^{3+}$, by a direct reaction of [Cu(2,4-C$_2$H$_4$)][BF$_4$] and PhSH in acetonitrile with BuNH$_2$·HCl as a mild reducing agent. The cluster displays architectural elements that were either rare or unknown in previously reported coinage-metal nanoclusters, including a core-shell structure with an unprecedented planar Cu$_{63}$ core and a hemispherical shell. Additionally, the aromatic ligands display disproportionate patterns and coverage, depending on whether they self-organize on the curved surface or on the planar surface of the cluster’s shell. Analysis and modeling of the weak intermolecular interactions between the surface ligands, such as π···π stacking and C–H···π interactions, indicates that they play an important role in directing and stabilizing the surface patterns. Therefore, the formation of the hemispherical structure of the Cu$_{63}$ cluster with a planar core should be considered a consequence of the synergistic effects between the surface-protecting ligands and the interstitial hydrides. This work paves the way for synthesizing high-nuclearity copper nanoclusters with previously undiscovered structures and reveals a new level of structural diversity that can exist in copper nanomaterials.

**EXPERIMENTAL SECTION**

**Materials.** Cuprous oxide (Cu$_2$O, ≥99.99% trace metals basis), tetrafluoroboric acid solution (HBF$_4$, 48 wt. % in water), Benzenethiol (PhSH, ≥98%), borane tert-butylamine complex (BuNH$_2$·HCl, ≥97%), tert-butylamine (BuNH$_2$, ≥98%), ammonium sulfate (NH$_4$)$_2$SO$_4$, ≥97%), sodium borodeuteride (NaBD$_4$, 98 atom % D, 90% (CP)), and HPLC-grade solvents (acetonitrile (CH$_3$CN), chloroform (CHCl$_3$), methanol (MeOH), tetrahydrofuran (THF), acetone and hexane) were purchased from Sigma-Aldrich. All chemicals were used directly without further purification. [Cu(2,4-C$_2$H$_4$)][BF$_4$] was
synthesized according to the literature procedure.\textsuperscript{56} "BuNH\textsubscript{2}BD\textsubscript{3} was synthesized by following the reported method\textsuperscript{56} using NaBD\textsubscript{4} as the deuteride source instead of NaBH\textsubscript{4}.

Synthesis and crystallization of Cu_{sun} and Cu_{sun}BD: [Cu\textsubscript{(CH\textsubscript{3}CN)}\textsubscript{2}]BF\textsubscript{4} (160 mg) was dissolved in 10 mL of CH\textsubscript{3}CN. Then, 30 µL of PhSH was added to the above solution. After vigorous stirring for 30 min, 200 mg of the reducing agent ("BuNH\textsubscript{2}BH\textsubscript{3}) dissolved in 3 mL of MeOH was rapidly added to the solution in one portion, and 3 mL of acetone was added to the above reaction solution. The color of the solution immediately changed to dark red. After stirring for ten minutes, the solvent was removed with a rotary evaporator, and the residue was dissolved in 10 mL of CH\textsubscript{3}Cl\textsubscript{2} to give a red solution.

Next, the above solution was divided into four equal parts, and 2 mL of hexane was added to each part. The final solution was kept in a sealed glass vial in a dark environment at room temperature. Six days later, ~6 mg of red rhombohedral crystals was obtained in ~95% yield (copper atom basis). Following the same synthetic method, "BuNH\textsubscript{2}BD\textsubscript{3} was used instead of "BuNH\textsubscript{2}BH\textsubscript{3} to synthesize the deuterated analogue (Cu_{sun}BD). The crystals of Cu_{sun} and Cu_{sun}BD were collected and kept in hexane for subsequent characterizations after washing with a solution of hexane:ethanol=2:1 (volume ratio).

ASSOCIATED CONTENT
Supporting Information. Instrumentation details, DFT results, UV-vis spectra, ESI-MS data, XPS spectra, hydroquinone reduction results, liquid-state NMR spectra, solid-state NMR spectra, and analyses of the crystal structures of Cu_{sun}. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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**Table of Content**

![Planar Cu_{10} core](image1.png)

![Cu_{101}](image2.png)