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Ligand Exchange-Induced Growth of an Atomically Precise Cu₂₉ Nanocluster from a Smaller Cluster

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ABSTRACT: The copper hydride nanocluster (NC) [Cu₂₉Cl₄H₂₂(Ph₂phen)₁₂]Cl (**2**; Ph₂phen = 4,7-diphenyl-1,10-phenanthroline) was isolated cleanly, and in good yields, by controlled growth from the smaller NC, [Cu₂₅H₂₂(PPh₃)₁₂]Cl (**1**), in the presence of Ph₂phen and a chloride source at room temperature. Complex **2** was fully characterized by single-crystal X-ray diffraction, XANES, and XPS, and represents a rare example of an $N^* = 2$ superatom. Its formation from **1** demonstrates that atomically precise copper clusters can be used as templates to generate larger NCs that retain the fundamental electronic and bonding properties of the original cluster. A time-resolved kinetic evaluation of the formation of **2** reveals that the mechanism of cluster growth is initiated by rapid ligand exchange. The slower extrusion of CuCl monomer, its transport, and subsequent capture by intact clusters, resemble elementary steps in the reactant-assisted Ostwald ripening of metal nanoparticles.

Introduction

Understanding the mechanisms of nanocluster (NC) formation and growth is an important step toward the tailoring of nanocluster structure and properties.¹⁻² An emerging method for controlling the size and structure of nanoclusters involves ligand exchange to induce a transformation from one stable cluster to another.³⁻⁶ Although such ligand exchange reactions are commonly used to introduce new functional groups onto the surface of clusters while preserving the original core size, they can also lead to changes in the shape and/or size of the metal core.^{3-5, 7} For example, exchange of the thiolate ligands in [Au₃₈(SCH₂CH₂Ph)₂₄] upon heating with HSC₆H₄-4-^tBu results in formation of a new, smaller cluster, [Au₃₆(SC₆H₄-4-^tBu)₂₄].⁸ Similarly, thiolate ligand exchange mediates the conversion of a Ag₄₄ cluster into a smaller Ag₂₅ cluster.⁹ In both of these examples, the change in cluster size likely occurs via thermally-induced disproportionation of an unstable intermediate in the presence of a very large excess of the new ligand, a process which has been called ligand-exchange-induced size/structure transformation (LEIST).¹⁻¹⁰ Generally speaking, however, the mechanisms of ligand exchange and cluster rearrangement are still poorly understood, and researchers are only now beginning to probe these questions.¹¹ Nevertheless, the resemblance to reactant-induced Ostwald ripening and disintegration of metal nanoparticles is intriguing.¹²⁻¹³ Moreover, examples are restricted to less reactive gold and silver NCs; copper NCs with metallic character are significantly rarer due to their much higher susceptibility to oxidation. In fact, to our knowledge, only two such

complexes are known, namely, [(Cp*AlCu)₆H₄] and [Cu₂₅H₂₂(PPh₃)₁₂]Cl (**1**).¹⁴⁻¹⁵

Herein, we describe the synthesis and structural characterization of the largest copper superatom known to-date, namely, the novel Cu₂₉ nanocluster, [Cu₂₉Cl₄H₂₂(Ph₂phen)₁₂]Cl (**2**). This material was generated via an unprecedented cluster growth mechanism, involving ligand exchange at room temperature, followed by CuCl monomer dissociation and capture by a previously assembled Cu₂₅ core. We also probe its electronic and geometric structure using X-ray absorption spectroscopy, and assess the rate law for its formation using time-resolved UV-vis spectroscopy.

Results and Discussion

Addition of 16 equiv of 4,7-diphenyl-1,10-phenanthroline (Ph₂phen) to a dark green solution of [Cu₂₅H₂₂(PPh₃)₁₂]Cl (**1**) in CH₂Cl₂ at room temperature causes an immediate color change to dark blue. Work-up of this solution after 15 h resulted in the isolation of a new mixed-valent copper hydride nanocluster, [Cu₂₉Cl₄H₂₂(Ph₂phen)₁₂]Cl (**2**), as a deep blue-black crystalline material in 84% yield (Scheme 1). While just 12 equiv Ph₂phen are formally required to form **2**, according to the stoichiometry of the reaction, the product was isolated in higher purity and yield when the reaction was performed in the presence of a small excess of the ligand. Reaction of **1** with 1,10-phenanthroline also yields a deep blue product, which is likely isostructural with **2** based on NMR spectral and ESI mass spectrometry data; however, single crystals of this complex were not obtained.

Scheme 1. Two Synthetic Routes for Cluster Expansion to Complex 2

Complex **2** crystallizes in the trigonal space group $P\bar{3}1c$ as a benzene solvate, $2 \cdot 16.5\text{C}_6\text{H}_6$ (Figure 1). In the solid state, it features a central core of 13 Cu atoms arranged in a centered-icosahedron. Notably, this is the same core structure found in the precursor cluster, **1**, which also features a central Cu atom with a coordination number of 12.¹⁵ The M_{13} icosahedral core is a common structural motif in nanoclusters, and is also found in $[\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-$,¹⁶⁻¹⁷ $[\text{Ag}_{21}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_{12}]^+$,¹⁸ $[\text{Au}_{13}(\text{PMe}_2\text{Ph})_{10}\text{Cl}_2]^{3+}$,¹⁹ and $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3+}$.²⁰ Comparison of **2** with $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3+}$ is particularly apt, as the two structures feature nearly identical spatial arrangements of their 29 metal atoms, despite very different ligand sets. Accordingly, we hypothesize that this structural arrangement is particularly stable.

The Cu_{13} core in **2** is connected, via Cu-Cu bonds, to four triangular $[\text{Cu}_4(\text{Ph}_2\text{phen})_3(\text{Cl})]$ motifs, which cap the icosahedron in a tetrahedral arrangement (Figures 1d and S26). This arrangement places 4 $[\text{CuCl}]$ units at the vertices of a tetrahedron (Figure 1c), while 12 $[\text{Cu}(\text{Ph}_2\text{phen})]$ units are distributed around the cluster in six π -stacked pairs (Figure 1b). The distance between the Ph_2phen ligands is 3.3 Å, in-line with typical π -stacking interactions.²¹⁻

²² As was observed for complex **1**, complex **2** occupies the high symmetry T point group. Interestingly, the majority of the Cu-Cu distances in **2** exhibit a relatively narrow range (2.537(3)-2.817(3) Å); only four of 96 Cu-Cu bonds (3.286-3.303 Å) fall outside this range (Figure 2b). This narrow distribution is reminiscent of the highly ordered structure of the bulk metal, although we note that the average Cu-Cu distance in **2** is somewhat longer (av. 2.65 Å) than the distance in bulk Cu (2.556 Å).²³ In contrast, complex **1** contains Cu-Cu bond distances that cover a much wider range (2.389(3)-3.037(3) Å) (Figure 2b), even though the arrangement of the Cu atoms in both nanoclusters is comparable.¹⁵ Most importantly, the isolation of **2** gives credence to the idea that small nanoclusters, such as **1**, can be used as templates for larger nanoclusters. Templated growth of nanoclusters has only been observed in a few instances, usually requiring significant thermal activation, and often occurs with major structural rearrangement.⁸

Figure 1. Ball and stick diagrams of complex **2**. The Cu_{13} centered-icosahedral cores are highlighted in blue. The remaining Cu atoms are shown in dark green. The N atoms are purple, the Cl atoms are lime green. All solvent molecules and outer-sphere counterions have been omitted for clarity. a) View down the C_3 axis, with C atoms depicted in wire frame. b) View down the C_2 axis, highlighting the π -stacking of the Ph_2phen ligands. C atoms are depicted in wireframe. c) Side view showing only the Cu and Cl atoms. d) Side view showing only the Cu, N, and Cl atoms.

In solution, complex **2** features a ^1H NMR spectrum consistent with the T symmetry observed in its solid-state structure, which requires that the six Ph_2phen backbone protons be inequivalent. For example, in CD_2Cl_2 , different resonances are assignable to the protons at the 2 and 9 positions of the Ph_2phen ligands, at 9.33 and 10.54 ppm, respectively. The ^1H NMR spectrum of **2** also features three broad resonances at 2.18, 2.56, and 3.44 ppm, which integrate for 4H, 12H, and 6H, respectively, and are assignable to 22 hydride ligands in three different chemical environments. A similar pattern is observed for **1**, and is further evidence that the core structure of complex **2** is essentially unchanged from that of **1**. This observation also suggests that the hydride positions in **2** are close to those predicted for complex **1**.¹⁵

Complex **2** features a signal at m/z 2979.803 in its electrospray ionization (ESI) mass spectrum, which corresponds to the $[\text{M-Cl}]^{2+}$ ion (Calcd m/z 2979.806), and a

signal at m/z 1974.878 which corresponds to the $[\text{M-2Cl}]^{3+}$ ion (Calcd m/z 1974.879). The parent $[\text{M}]^+$ ion was not detected, presumably due to the lability of the coordinated chlorides in the gas phase. The synthesis and characterization of the deuteride analog, **2-d₂₂**, also supports our proposed formulation. In particular, complex **2-d₂₂** features singlets at 2.30, 2.71, and 3.69 ppm in its ^3H NMR spectrum, in a 4:12:6 ratio, respectively. In addition, complex **2-d₂₂** features a signal at m/z 2990.869 in its ESI mass spectrum, which corresponds to the $[\text{M-Cl}]^{2+}$ ion (Calcd m/z 2990.875), and a signal at m/z 1982.249 which corresponds to the $[\text{M-2Cl}]^{3+}$ ion (Calcd m/z 1982.258). These values represent a shift of 22 atomic mass units relative to the signals observed for **2-h₂₂**. Finally, two of the Cu atoms in complex **2** must have a formal Cu(0) oxidation state to maintain charge balance, making complex **2** only the third structurally-characterized Cu nanocluster with partial Cu(0) character.¹⁴⁻¹⁵ Complex **2** can also be de-

scribed as an $N^* = 2$ superatom with a closed-shell $1S^2$ configuration.²⁴ This is a rare electronic structure with only a handful other well-defined examples, including $\text{Ag}_{14}(\text{SC}_6\text{H}_3\text{F}_2)_{12}(\text{PPh}_3)_8$, $\text{Ag}_{16}(\text{SC}_6\text{H}_3\text{F}_2)_{14}(\text{DPPE})_8$ (DPPE = 1,2-bis(diphenylphosphino)ethane), $\text{Au}_n(\text{SR})_9$, and $\text{Au}_{15}(\text{SR})_{13}$.^{2, 25-27}

We also briefly probed the chemical properties of complex **2**. It is soluble in CH_2Cl_2 and PhCl, sparingly soluble in MeCN, and insoluble in THF, Et_2O , and nonpolar solvents. Complex **2** is stable as a PhCl solution for at least 2 d at room temperature, but solutions of **2** in CH_2Cl_2 gradually decompose over the same time period, changing in color from deep blue to dark brown. This is likely due to oxidation by the solvent, which results in formation of copper chloride-containing decomposition products.⁶ As a CH_2Cl_2 solution, complex **2** is stable in the presence of 40 equiv. of water for at least 5 h, but it is highly O_2 -sensitive, and decomposes completely within 10 min upon exposure to air. The enhanced O_2 sensitivity of **2**, relative to thiol-passivated Ag and Au NCs, is a consequence of the much higher reactivity of the Cu-H bond,²⁸ which is partially rooted in the large enthalpic driving force for H_2O formation. While this difference makes copper hydride NCs more challenging to handle, it also provides potential opportunities for catalysis, as copper hydrides are known to promote a wide variety of organic transformations.²⁸

The effect of Cu oxidation state(s) and cluster nuclearity is evident in the Cu K-edge X-ray absorption near-edge spectra (XANES) of **1** and **2** (Figure 2a).¹⁵ Both the maximum absorbance at the edge (i.e., the whitenline) and the peak superimposed on the edge are more intense in the spectrum of **2** relative to **1**. In the post-edge region, both **1** and **2** show weaker multiple-scattering intensity than Cu foil, consistent with their small cluster sizes. At 8979.5 eV, the edge position of **2** is very similar to that for **1** and resides between values measured for Cu(0) in the bulk foil (8979.0 eV) and Cu(I) in clusters such as $[\text{CuH}(\text{PPh}_3)]_6$ (8980.0 eV) and $[\text{CuCl}(\text{PPh}_3)]_4$ (8980.9 eV).¹⁵ This is consistent with an average Cu oxidation state for **2** between 0 and +1 (Table S2). Likewise, the XPS Auger parameter, at 1848.9 eV, is intermediate between values for bulk Cu(0) (1851.2 eV) and those for the hexanuclear and tetranuclear Cu(I) clusters (1848.6 and 1847.4 eV, respectively), in agreement with partial Cu(0) character for **2**. A similar observation was made previously for **1**.¹⁵ The N:Cu ratio of **2** determined by XPS, 0.82, is the same as the expected value based on the crystal structure (Table S4).

Interestingly, the narrow range of Cu-Cu distances in complex **2** is clearly manifested in its extended X-ray absorption fine structure (EXAFS) (Figure 2b; see Figure S28 for full EXAFS curves). The FT magnitude shows a maximum at 2.2 Å in non-phase-corrected R -space, with a low- R shoulder. No long-range scattering is visible, as is typical for very small nanoclusters. In contrast, complex **1** has a much broader and less symmetrical peak centered at 2.0 Å, consistent with its wider range of Cu-Cu distances. A single Cu-Cu path, in conjunction with a Cu-N path, suffices to achieve a satisfactory curvefit to the EXAFS of **2**

(Figure 2c), while the curvefit to the EXAFS of **1** required two different Cu-Cu shells in addition to the Cu-P path.¹⁵ The former curvefit gives an average Cu-Cu single-scattering pathlength of 2.567(3) Å for **2**, close to the value derived from single-crystal X-ray diffraction (2.65 Å), while the refined average coordination number ($N = 6.8 \pm 0.6$) is close to the expected value (7.5). Thus, XANES and EXAFS are sufficiently sensitive to discriminate between these closely related nanoclusters.

Figure 2. a) Comparison of Cu K-edge XANES profiles for Cu foil and nanoclusters **1** and **2**. b) Comparison of Cu K-edge EXAFS for nanoclusters **1** and **2** (phase-corrected FT magnitude: top), as well as distributions of Cu-Cu bond distances based on single-crystal X-ray diffraction (middle and bottom). c) EXAFS curvefit (lines) for **2**, showing data (circles) as the FT magnitude and its imaginary component in non-phase-corrected R -space. Data for **1** taken from Ref. 15.

Formation of **2** by cluster expansion of **1** requires both complete exchange of 12 Ph_3P ligands by 12 Ph_2phen ligands, and addition of four “CuCl” units to the Cu_{25} core. We hypothesize that this process occurs in two stages. First, rapid ligand exchange with Ph_2phen results in formation of $[\text{Cu}_{25}\text{H}_{22}(\text{PPh}_3)_{12-n}(\text{Ph}_2\text{phen})_n]\text{Cl}$. This unstable intermediate then reacts sequentially with four “CuCl” units to generate complex **2**. The “CuCl” units are presumably derived from a reaction between a sacrificial molecule of $[\text{Cu}_{25}\text{H}_{22}(\text{PPh}_3)_{12-n}(\text{Ph}_2\text{phen})_n]\text{Cl}$ and the CH_2Cl_2 solvent, releasing “CuCl” monomers and forming CH_3Cl . A similar chloride-hydride metathesis process occurs during the formation of $[\text{Cu}_{14}\text{H}_{12}(\text{phen})_6(\text{PPh}_3)_4][\text{Cl}]_2$ from $[(\text{PPh}_3)\text{CuH}]_6$ and phen in CH_2Cl_2 , wherein the solvent provides the required Cl^- counterions, and forms CH_3Cl as a by-product.⁶ Importantly, only a small fraction of $[\text{Cu}_{25}\text{H}_{22}(\text{PPh}_3)_{12-n}(\text{Ph}_2\text{phen})_n]\text{Cl}$ is required to form the required “CuCl” monomers, since just one cluster can supply 25 equiv of “CuCl”.

In view of the presence of excess Ph_2phen and un-ligated Ph_3P in the reaction mixture, we hypothesized that a

much smaller mixed-ligand $\text{Ph}_2\text{phen}/\text{PPh}_3$ coordination complex, such as $[(\text{Ph}_2\text{phen})(\text{PPh}_3)\text{CuCl}]$ (**3**), acts as the “CuCl” carrier during formation of **2**. To confirm its viability in this role, $[(\text{Ph}_2\text{phen})(\text{PPh}_3)\text{CuCl}]$ (**3**) was synthesized independently by the reaction of CuCl, PPh_3 and Ph_2phen , and was isolated in 97% yield (see SI for full characterization). The self-assembly of complex **3** from this mixture, as well as its isolation in nearly quantitative yield, are consistent with the hypothesis that it forms readily *in situ* and can act as a “CuCl” carrier. In further support of its role in the cluster expansion, reaction of **1** with 4 equiv of complex **3** and 11 equiv Ph_2phen , in chlorobenzene resulted in formation of complex **2**, recovered in 67% yield after work-up (Scheme 1). This material is spectroscopically identical to that obtained by the simple ligand exchange method described above; however, the direct use of **3** made it possible to form **2** in the absence of CH_2Cl_2 as a chloride source.

To further probe the transformation of complex **1** to **2**, and to test the hypothesis that $[(\text{Ph}_2\text{phen})(\text{PPh}_3)\text{CuCl}]$ (**3**) is an intermediate in the reaction, we monitored the formation of **2** using UV-vis spectroscopy. In contrast to polydisperse nanoparticles, atomically-precise nanoclusters show discrete bands in their UV-vis spectra.¹⁰ Complex **1** in CH_2Cl_2 features a prominent band at 460 nm, as well as a broad band at 615 nm with a shoulder at 675 nm (Figure S30). Ligand exchange upon addition of 2, 4 or 8 equiv of **3** with 11 equiv of Ph_2phen (both relative to 1 equiv of complex **1**, ca. 0.05 mM) at 25 °C induced a rapid color change of the solution to blue-black, concomitant with the appearance of overlapping bands at ca. 395, 575, 725, and 900 nm (Figure S30).

The kinetics of the subsequent conversion of **1** to **2** were monitored at 575 nm (Figure 3). In the absence of added **3** (black points), the cluster rearrangement reaction is slow, and the reaction profile is pseudo-zeroth-order (Figures 3 and S31). Presumably, ligand exchange (eq 1) results in slow extraction of monomer **3** from **1** to give a less stable nanocluster (e.g., Cu_{24}), via a process that also involves the solvent, eq 2.

The rate is much faster in the presence of added **3**, and accelerates as $[\mathbf{3}]$ increases. The quality of the non-linear curve fits of the first-order integrated rate equation to the kinetic profiles improves as the $[\mathbf{3}]/[\mathbf{1}]$ ratio increases, as expected since the reaction conditions become closer to pseudo-first-order. The dependence of k_{obs} on $[\mathbf{3}]$ is linear (Figure 3 inset and Table S6). These findings suggest a mechanism in which **1** undergoes initial, rapid ligand exchange in a pre-equilibrium step (eq 1), followed by association with monomer **3** to give a larger nanocluster (i.e., Cu_{26}) in a kinetically relevant capture step such as eq 3.

Figure 3: Kinetic profiles for the transformation of 0.05 mM **1** to **2** in CH_2Cl_2 at 25 °C, recorded with 15 equiv Ph_2phen and no added $[\text{Cu}(\text{Ph}_2\text{phen})(\text{PPh}_3)\text{Cl}]$ (**3**) (black points), or 11 equiv Ph_2phen and variable amounts of added $[\text{Cu}(\text{Ph}_2\text{phen})(\text{PPh}_3)\text{Cl}]$ (**3**) (colored points). Lines are curvefits to the first-order integrated rate law. The inset shows the linear dependence of the pseudo-first-order rate constants on the concentration of added **3**.

To assess the reaction order with respect to Ph_2phen , kinetic profiles were recorded with 8, 14, or 17 equiv of Ph_2phen and a constant amount of **3** (4 equiv with respect to **1**) at 25 °C. The pseudo-first-order rate constants k_{obs} correlate linearly with the concentration of added Ph_2phen (Figure S32 and Table S5), indicating that the rate law contains a term that is first-order in both the chelating ligand and the monomer **3**. The empirical rate law is shown in eq 4.

$$d[\mathbf{2}]/dt = k_0 + k_1[\mathbf{1}][\mathbf{3}][\text{Ph}_2\text{phen}] \quad (4)$$

A similar series of kinetics experiments was repeated at 10 °C in order to estimate the apparent activation energy associated with the rate constant k_1 (Figure S33). Preliminary Arrhenius analysis yields $E_a \sim 72$ kJ/mol. This value undoubtedly represents several elementary steps involving ligand dissociation/association, and reorganization/redistribution of Cu-Cu bonds. For comparison, Jin and co-workers reported that the activation energy for the disproportionation of a Au_{38} cluster into Au_{36} and Au_{40} is 94 kJ/mol.⁸

Summary

In summary, we describe the synthesis of a new Cu_{29} nanocluster via a unique mechanism of cluster growth initiated by ligand exchange and involving CuCl monomer formation, transport, and addition. This mechanism could be applicable to other nanocluster systems, and suggests a new strategy to manipulate metal NCs. Additionally, our results reveal the role of a well-defined carrier molecule that mediates the growth process. This study also demonstrates that detailed spectroscopic and kinetic assessments can be obtained for well-defined nanoclusters, and should be highly amenable to first-principles

computational analysis.¹⁵ Such studies promise to provide the first quantitative descriptions of nanocluster growth kinetics, in contrast to polydisperse nanoparticle systems whose descriptions remain largely qualitative despite advances in *in situ* observations.¹²

In future studies, X-ray absorption spectroscopy could provide important information about transient species, nanoclusters generated *in situ*, and supported nanoclusters for which single-crystal X-ray diffraction is not possible. More detailed measurements will likely yield information that can be used to understand and predict the driving forces and barriers for cluster rearrangement, and for benchmarking computational models.²⁹ Ultimately, we expect that a better understanding of cluster behavior and structure will advance the design of nanocluster-based materials for technological applications in sensing, optical imaging, nanomedicine and catalysis.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic details (as a CIF file), experimental details, spectral data, and additional figures and tables. 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 interests.

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