# Synthesis and Characterization of "Atlas-sphere" Copper Nanoclusters: New Insights into the Reaction of Cu<sup>2+</sup> with Thiols

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Supporting Information Placeholder

**ABSTRACT:** Thiolates are a widely used ligand class for the stabilization of M(0)-containing gold and silver nanoclusters. Curiously, though, very few thiolate-stabilized Cu nanoclusters are known. Herein, we report an examination of the reactivity of RSH (R = CH<sub>2</sub>CH<sub>2</sub>Ph, *n*-Bu, *n*-C<sub>12</sub>H<sub>25</sub>) with Cu<sup>2+</sup> under anhydrous conditions. These reactions result in formation of fluorescent "Atlas-sphere"-type copper-thiolate nanoclusters, including  $[Cu_{12}(SR')_6Cl_{12}][(Cu(R'SH))_6]$  (2,  $R' = {}^{n}Bu$ ) and  $[H(THF)_2]_2[Cu_{17}(SR'')_6Cl_{13}(THF)_2(R''SH)_3]$  (3, R' CH2CH2Ph), which were characterized by X-ray crystallography, ESI-MS, NMR spectroscopy, as well as XANES and EXAFS. Consistent with our X-ray crystallographic results, the edge energies of 2 and 3 suggest they are constructed exclusively with Cu(I) ions. Similarly, EXAFS of 2 and 3 reveal long Cu-Cu pathlengths, which is also consistent with their X-ray crystal structures. Given these results, as well as past work on  $Cu^{2+}$ /thiol reactivity, we suggest that Cu(0) is unlikely to be formed by reaction of Cu<sup>2+</sup> with a thiol, and that previous reports of Cu(0)-containing nanoclusters synthesized by reaction of Cu<sup>2+</sup> with thiols are likely erroneous.

### Introduction

The past decade has seen a dramatic increase in the number of reported atomically precise nanoclusters (APNCs) of gold and silver.<sup>1</sup> Many of these APNCs have been characterized by X-ray crystallography, giving researchers a level of structural detail that is not available for traditional nanoparticles. For Ag and Au, the most common capping ligands are thiolates (RS<sup>-</sup>) (R = alkyl, aryl). For example, one of the first structurally characterized Au APNCs, [Au25(SCH2CH2Ph)18], features phenylethylthiolate capping ligands.<sup>2-3</sup> Other notable thiolate-stabilized Au APNCs include [Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub>], [Au144(SCH2CH2Ph)60], [Au<sub>246</sub>(SC<sub>6</sub>H<sub>4</sub>-*p*-Me)<sub>80</sub>], and Au<sub>279</sub>(SC<sub>6</sub>H<sub>4</sub>-p-Bu)<sub>84</sub>.<sup>4-7</sup> Similarly, many of the first structurally characterized Ag APNCs also featured thiolate ligands, including  $[Ag_{44}(p-MBA)_{30}]^{4-}$  (p-MBA = para-mercaptobenzoic acid) and [Ag25(SCH2CH2Ph)18]-.8-10 As seen in these aforementioned examples, both alkyl- and aryl thiolates are effective at stabilizing Ag and Au APNCs. The ubiquitous use of thiolates for this purpose is likely related to the strength of the M-S bond,<sup>11</sup> which protects the APNCs against agglomeration and unwanted reactivity. As a result, these materials have been proposed for a variety of applications for which high stability is desired, including *in vivo* chemical sensing and drug delivery.<sup>1</sup>

Given this context, it is surprising that Cu(0)-containing, thiolate-stabilized Cu APNCs are essentially unknown, and of the few Cu APNCs that have been reported, most have only been partially characterized.<sup>12-14</sup> For example, Mukherjee and coworkers synthesized a glutathione-stabilized Cu APNC with the formula [Cu15(GSH)4].15 This material was characterized by TEM, MALDI-TOF mass spectrometry, and UV-vis spectroscopy, but a single-crystal X-ray structure was not forthcoming. Similarly, Chang and co-workers reported the synthesis of a mixture of mercaptobenzoic acid-stabilized Cu nanoclusters, but these materials were not structurally characterized.<sup>16</sup> In contrast, structurally-characterized mercaptobenzoic acid-stabilized APNCs of both Ag and Au are well known.<sup>1</sup> Cu APNCs of aryl thiolates have also been reported, such as [Cu<sub>9</sub>(SC<sub>6</sub>H<sub>4</sub>p-F)7] and [Cu9(SC6H4-p-Br)6], but again structural characterization by X-ray crystallography has remained elusive.<sup>17</sup> Finally, it is worth noting that a 2011 report of a thiolate-stabilized  $Cu_8$ nanocluster,  $[Cu_8(MPP)_4]$  (HMPP = 2-mercapto-5-*n*-propylpyrimidine), was recently found to be erroneous.<sup>18-19</sup>

In 2015, Zhang and co-workers reported the synthesis of a mixed-valent Cu-thiolate APNC Cu<sub>14</sub>(SR)<sub>10</sub> (R = C<sub>12</sub>H<sub>25</sub>), which was formed by reaction of CuCl<sub>2</sub> with excess RSH in dibenzyl ether.<sup>20</sup> Under these conditions, the thiol acts as both the capping ligand and the reductant. Cu<sub>14</sub>(SR)<sub>10</sub> was characterized by UV-vis and fluorescence spectroscopies, TGA, and TEM, amongst other techniques. While its exact structure could not be verified by single-crystal X-ray diffraction, the authors use mass spectrometry and DFT analysis to support their proposed formulation. Significantly, this Cu APNC was reported to have attractive photo-physical properties,<sup>21-23</sup> prompting speculation that it could be incorporated into light emitting diodes and displays.<sup>17</sup>

  $[Cu_{53}(CF_3CO_2)_{10}(C=C'Bu)_{20}Cl_2H_{18}]^{+.24, 26-30}$  Cu<sub>14</sub>(SR)<sub>10</sub> would also be an exceptionally rare example of a copper superatom with  $N^* = 4$ , which is not a magic number.<sup>20</sup> While non-magic number copper superatoms are known, such as  $[Cp^*_{12}Cu_{43}Al_{12}]$ , their anticipated lower stability makes them unusual.<sup>1, 19, 29</sup>

Consequently, we attempted to remake Cu<sub>14</sub>(SR)<sub>10</sub> in an effort to further investigate its structure. Surprisingly, we found that the reaction of CuCl<sub>2</sub> with RSH ( $R = C_{12}H_{25}$ ) does not result in a Cu APNC with Cu(0) character. Instead, the product is most likely a Cu(I)-containing "Atlas-sphere"-type thiolate nanocluster. Our conclusion is supported by a comparative synthetic and spectroscopic study, which includes analysis by Xray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS). During the course of this work, we also the synthesized and structurally characterized two other Cu(I) thiolate-containing clusters, <sup>n</sup>Bu)  $[Cu_{12}(SR')_6Cl_{12}][(Cu(R'SH))_6]$ (R' = and [H(THF)<sub>2</sub>]<sub>2</sub>[Cu<sub>17</sub>(SR'')<sub>6</sub>Cl<sub>13</sub>(THF)<sub>2</sub>(R''SH)<sub>3</sub>] (R CH<sub>2</sub>CH<sub>2</sub>Ph) using similar conditions to those reported by Zhang and co-workers.20

## **Results and Discussion**

Attempted Synthesis of  $Cu_{14}(SR)_{10}$  (R =  $C_{12}H_{25}$ ). Cu<sub>14</sub>(SR)<sub>10</sub> was reportedly formed by reaction of CuCl<sub>2</sub>·2H<sub>2</sub>O (1 equiv) with 1-dodecanethiol (22 equiv) in dibenzyl ether (6 mL) (Scheme 1). A yield was not reported and the color of the material was not described, but photographs provided in the Supporting Information show that the solid is a pale-yellow powder.<sup>20-21</sup> The solubility of this material was also not explicitly discussed, but on the basis of the experimental description it appears to be insoluble in both CHCl<sub>3</sub> and acetone.

Zhang and co-workers characterized their material using a variety of methods, including UV-vis and emission spectroscopies, as well as mass spectrometry. The Cu<sub>14</sub>(SR)<sub>10</sub> formulation was proposed primarily on the basis of the MS data, however neither an exact mass match nor an analysis of the isotope pattern was provided.<sup>20-21</sup> The UV-vis data of the isolated material revealed the presence of two absorption bands at 275 and 358 nm. The fluorescence spectrum ( $\lambda_{ex} = 365$  nm) showed a weak emission at approximately 380 nm.

#### Scheme 1. Synthetic Procedure Used to Prepare Cu<sub>14</sub>(SR<sub>10</sub>)



We attempted to repeat the synthesis of  $Cu_{14}(SR)_{10}$ , using the originally reported procedure with a few minor modifications. In particular, we used anhydrous  $CuCl_2$  in place of  $CuCl_2 \cdot 2H_2O$ ,<sup>31</sup> we did not sonicate our  $CuCl_2$  suspension, and we performed the reaction at room temperature. We believe that these minor changes should not affect the product speciation; however, they could affect the rate of reaction by modifying the solubility and grain size of the  $CuCl_2$  starting material. The reaction generally proceeded as originally described (Scheme 1). Thus, addition of  $CuCl_2$  (1 equiv) to dibenzyl ether (2 mL) at room temperature resulted in formation of a pale brown slurry. Addition of 1-dodecanethiol (4 equiv) to this suspension resulted in dissolution of the brown solid over the course of 20 min, concomitant with the deposition of a very pale

gray solid, which is similar in appearance to the material reported by Zhang and co-workers.<sup>20</sup> The solid was then collected on a fritted glass filter, and rinsed with hexanes to give 1 as an off-white solid (Figure S29). We also performed the reaction in THF. In this solvent, addition of 1-dodecanethiol to the slurry of CuCl<sub>2</sub> in THF initially resulted in dissolution of all the solid over the course of 2 min, concomitant with formation of a clear, pale-yellow solution. However, upon further stirring, a very pale-yellow powder began to precipitate from the solution (Figure S30). After 20 min of stirring, this solid was collected on a fritted glass filter and rinsed with several portions of hexanes to give 1 as a very pale yellow powder. Whether prepared from dibenzyl ether or THF, complex 1 is insoluble in alkanes, diethyl ether, benzene, toluene, THF, CH2Cl2, chloroform, MeCN, DMSO, DMF, MeOH, EtOH, and water. While complex 1 is also insoluble in pyridine, it does appear to very slowly react with this solvent.

To better ascertain the reaction stoichiometry, we collected the colorless filtrate from the THF reaction mixture and removed the volatiles *in vacuo* to yield a colorless oil. A <sup>1</sup>H NMR spectrum of this colorless oil, recorded in CD<sub>2</sub>Cl<sub>2</sub> (Figure S8), reveals the presence of unreacted 1-dodecanethiol, as well as di(1-dodecane)disulfide.<sup>32</sup> These observations are consistent with the proposed reaction stoichiometry of Zhang and coworkers, who also noted the reduction of the Cu(II) ions via thiol oxidation.

A diffuse reflectance spectrum of solid **1** features the onset of an absorption band at ca. 425 nm (Figure 1, black trace). A fluorescence spectrum of the same material excited at 365 nm reveals a very broad emission centered at 510 nm (Figure 1, red trace). These data are broadly consistent with the spectra reported by Zhang and co-workers. For example,  $Cu_{14}(SR)_{10}$  was reported to have an absorption band centered at 368 nm,<sup>20</sup> along with emission peaks centered at 490 or 550 nm (depending on the method of sample preparation). Overall, the similarity of our spectroscopic results with those previously reported by Zhang, along with the similar physical descriptions of the two materials, leads us to believe that we are making the same material. The TGA trace recorded for **1** is also a close match with that reported previously for  $Cu_14(SR)_{10}$  (Figure S31).<sup>20</sup>



**Figure 1.** Solid-state absorbance (black) and emission (red,  $\lambda_{ex}$  = 365 nm) spectra for complex 1, synthesized from THF.

Finally, we recorded an X-ray photoelectron spectrum of cluster **1** to confirm the Cu oxidation state and determine its elemental composition. Specifically, the spectrum features two prominent peaks at 932.70 and 952.70 eV, which are attributable to the Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  binding energies, respectively. These values are similar to the binding energies reported for

other Cu(I)-containing materials.<sup>24, 33</sup> Unfortunately, the similarity of Cu(I) and Cu(0) binding energies<sup>34</sup> generally makes it difficult to discriminate between these two states, and so we cannot rule out the presence or absence of Cu(0) in this sample. Nonetheless, the absence of satellite peaks in this region of the spectrum is consistent with absence of Cu(II). Moreover, the Cu LMM transitions for 1 appear at 918.3, 915.5, and 911.6 eV. These values are also consistent with the presence of Cu(I), in multiple chemical environments. As with the Cu 2p binding energies, it is difficult to use the Cu LMM data to discriminate between the Cu(0) and Cu(I) states. That said, our Cu LMM data closely match that originally reported for Cu<sub>14</sub>(SR)<sub>10</sub>, which exhibits transitions at ca. 918 and 915 eV.<sup>20</sup> Curiously, our XPS spectrum also reveals the presence of Cl, as revealed by the Cl 2s and Cl 2p<sub>3/2</sub> peaks at 269.7 and 199.2 eV (Figure S21 and S25).<sup>34</sup> According to XPS data, the Cu:S:Cl ratio is approx. 2:2:1. Significantly, these data are not consistent with the original Cu<sub>14</sub>(SR)<sub>10</sub> formulation, which should not contain Cl<sup>-</sup>, but are in-line with our findings from a comparative synthetic study using different thiols (see below). To be fair, though, Zhang and co-workers may not have tested their material for the presence of Cl<sup>-</sup>. Nonetheless, on the basis of these results, we believe that complex 1 is not a partially-metallic, mixed-valent Cu nanocluster. Instead, we believe that this material is likely an "Atlas-sphere" [Cu<sub>12</sub>(SR)<sub>6</sub>]<sup>6+</sup>-type cluster. That is, it does not have any Cu(0) character but instead contains exclusively Cu(I). Our evidence to support this conclusion is outlined in the next sections.

Synthesis of  $[Cu_{12}(SR')_6Cl_{12}][(Cu(R'SH))_6]$  (R' = "Bu). The insolubility of 1 greatly limited our ability to confirm its formulation. Therefore, we attempted to generate a more tractable material by substituting the 1-dodecanethiol ligand for an aliphatic thiol that was more amenable to crystallization, yet similar in structure and reducing ability (Scheme 2).<sup>35</sup> Thus, reaction of a slurry of CuCl<sub>2</sub> (1 equiv) in THF (2 mL) with *n*-butylthiol (5 equiv) at room temperature immediately results in dissolution of the CuCl<sub>2</sub>, concomitant with the generation of a bright yellow solution. Work-up of the reaction mixture after 20 min resulted in the isolation of pale yellow crystals of the Cu(I) nanocluster,  $[Cu_{12}(SR')_6Cl_{12}][(Cu(R'SH))_6]$  (2, R' = "Bu), in 90% yield.

## Scheme 2. Synthesis of 2.



Complex 2 crystallizes in the triclinic space group  $P\overline{1}$  (Figure 2). It features a [Cu<sub>12</sub>(SR')<sub>6</sub>]<sup>6+</sup> "Atlas-sphere" core (Figure 2a), which has been observed for several other Cu(I) thiolate clusters.<sup>12, 36-39</sup> Within the Cu<sub>12</sub>S<sub>6</sub> core, each Cu occupies the vertex of a regular cuboctahedron, while each thiolate ligand is bound in a  $\mu_4$  fashion and occupies one of the six square faces of the cuboctahedron. The Cu-Cu distances range from 2.6524(7) to 3.7110(8) Å, while the Cu-SR' distances range from 2.225(2) to 2.276(1) Å. Both of these ranges are comparable to those seen in other [Cu<sub>12</sub>(SR)<sub>6</sub>]<sup>6+</sup>-containing clusters.<sup>12, 36-39</sup> Each of the 12 Cu atoms in the "Atlas-sphere" core is also coordinated to a Cl<sup>-</sup> ligand. Six additional Cu<sup>+</sup> ions are bound to the outer surface of the cluster, via bridging interactions with the Cl<sup>-</sup> ions. Two of these outer Cu<sup>+</sup> ions are each coordinated to a single thiol ligand, while the remaining four Cu<sup>+</sup> ions are each coordinated to two thiol ligands, four of which originate from an adjacent cluster. These bridging interactions give rise to a laddertype coordination polymer bridging through two µ2-HSR linkages (Figure 2c).<sup>38</sup> The average Cu-Sthiol distance is 2.30 Å (range: 2.257(1) - 2.346(2) Å), which is slightly longer than the Cu-thiolate distance, as expected.

The <sup>1</sup>H NMR spectrum of **2** in THF- $d_8$  (Figure S2) features resonances at 3.26 and 2.53 ppm, assigned to the  $\alpha$ -CH<sub>2</sub> resonances of the six  $\mu_4$ -S<sup>n</sup>Bu ligands and the six <sup>n</sup>BuSH ligands, respectively. These resonances are present in a 1:1 ratio, consistent with the solid-state structure. Also present in this spectrum is a broad singlet at 1.85 ppm, assigned to the SH proton of the six "BuSH ligands. The ESI-MS of 2, recorded in THF in negative ion mode, features a major peak at m/z = 2039.9023, which corresponds to the fragment  $[Cu_{17}(SR')_6Cl_{12}]^-$  (calcd m/z= 2039.6666) (Figure 3). Several other peaks are also present in this spectrum. Each of these peaks is related to the parent ion by loss/gain of CuCl (m/z = 99). These data suggest that the  $[Cu_{12}(SR')_6Cl_{12}]^{6-}$  core is relatively stable, but that the six outer Cu<sup>+</sup> ions and coordinated thiol ligands are quite labile. Interestingly, an ESI-MS signal for 2 was only observed upon addition of [NEt4][Cl] to the ESI-MS sample. It was observed previously that addition of salts to a nanocluster sample can facilitate transfer of material into the gas phase during the MS analysis.<sup>40</sup> Finally, a UV-vis spectrum of 2 in THF (Figure S16) reveals the presence of an absorption band at 370 nm. The spectrum is qualitatively similar to the spectrum recorded for Cu<sub>14</sub>(SR)<sub>10</sub>,<sup>20</sup> providing further support for the structural similarity of that material and 2. The fluorescence spectrum of solid 2 ( $\lambda_{ex} = 365$ nm) reveals a broad emission peak at 585 nm (Figure S19).



**Figure 2.** Ball-and-stick diagram showing a) the  $[Cu_{12}(SR')_6Cl_{12}]^6$  core, b) the structure of the monomeric unit, and c) the polymeric structure of **2** (hydrogen atoms omitted for clarity). Color legend: orange, Cu; yellow, S; green, Cl; gray, C.



Figure 3. Partial ESI-MS of complex 2 in negative ion mode. Assignments: m/z = 2039.9023 [Cu<sub>17</sub>(SR')<sub>6</sub>Cl<sub>12</sub>] (calcd m/z =

2039.6666), m/z = 2139.7942 [Cu<sub>18</sub>(SR')<sub>6</sub>Cl<sub>13</sub>]<sup>-</sup> (calcd m/z = 2139.5649), m/z = 1940.9977 [Cu<sub>16</sub>(SR')<sub>6</sub>Cl<sub>11</sub>]<sup>-</sup> (calcd m/z = 1940.7682), m/z = 1842.0930 [Cu<sub>15</sub>(SR')<sub>6</sub>Cl<sub>10</sub>]<sup>-</sup> (calcd m/z = 1841.8719), m/z = 1744.175 [Cu<sub>14</sub>(SR')<sub>6</sub>Cl<sub>9</sub>]<sup>-</sup> (calcd m/z = 1743.9734).

To better understand the stoichiometry of the transformation, the reaction of CuCl<sub>2</sub> with "BuSH (5 equiv) was monitored by <sup>1</sup>H NMR spectroscopy (Figure S4). Addition of thiol to a THF $d_8$  slurry of CuCl<sub>2</sub> results in the rapid dissolution of all solids and the formation of a bright yellow solution. After 20 min, the <sup>1</sup>H NMR spectrum of this solution revealed a resonance at 3.24 ppm, assigned to the  $\alpha$ -CH<sub>2</sub> resonance of the six  $\mu$ <sub>4</sub>-S<sup>*n*</sup>Bu ligands in 2, a resonance at 2.68 ppm, assigned to the  $\alpha$ -CH<sub>2</sub> resonance of di-n-butyl disulfide, and a broad resonance at 8.56 ppm, assigned to HCl. Integration of the methylene resonances against an internal standard (hexamethyldisiloxane) indicates that 2 was formed in 99% yield, while only 0.5 equiv of di-nbutyl disulfide was generated per CuCl<sub>2</sub>. Similarly, integration of the HCl resonance indicates that 1.3 equiv of HCl is formed relative to the initial amount of CuCl<sub>2</sub>. Importantly, these amounts of disulfide and HCl are consistent only with reduction of Cu(II) to Cu(I) and formation of 2. If  $Cu_{14}(SR)_{10}$  were to be formed in this transformation, we would expect 0.64 equiv of di-n-butyl disulfide and 2.0 equiv of HCl to be formed instead.

We also briefly examined the chemical properties of complex 2. Complex 2 is insoluble in alkanes, Et<sub>2</sub>O, benzene, toluene, CH<sub>2</sub>Cl<sub>2</sub>, and MeCN. It is soluble in THF, although it partially decomposes if left in solution at room temperature, as evidenced by the gradual bleaching of the pale-yellow color in conjunction with the deposition of a copious amount of white powder, presumably CuCl. This process occurs over the course of 24 h. Finally, complex **2** reacts immediately upon dissolution in pyridine, to form [CuCl(pyridine)<sub>3</sub>] (**4**) as the only isolable product. This complex can be isolated in 68% yield (based on Cl<sup>-</sup>) after work-up.<sup>41</sup> The isolation of **4** from the reaction mixture demonstrates that, under the appropriate conditions, the "Atlas-sphere" core is susceptible to disassembly.

Synthesis of  $[H(THF)_2]_2[Cu_{17}(SR'')_6Cl_{13}(THF)_2(R''SH)_3]$ (R'' = CH<sub>2</sub>CH<sub>2</sub>Ph). To further understand the reactivity of Cu(II) with thiols, we explored the reaction of CuCl<sub>2</sub> with 2-phenylethanethiol. This specific thiol was chosen because it is widely used in the synthesis of Ag and Au APNCs,<sup>1</sup> yet an isolable 2-phenylethylthiolate-containing Cu APNC has so far remained elusive. Thus, reaction of a slurry of CuCl<sub>2</sub> (1 equiv) in THF with 2-phenylethanethiol (4 equiv) at room temperature immediately generates a bright yellow solution concomitant with dissolution of the CuCl<sub>2</sub> (Scheme 3). Work-up of the reaction mixture after 20 min resulted in pale yellow crystals of the Cu(I) nanocluster [H(THF)<sub>2</sub>]<sub>2</sub>[Cu<sub>17</sub>(SR'')<sub>6</sub>Cl<sub>13</sub>(THF)<sub>2</sub>(R''SH)<sub>3</sub>] (R'' = CH<sub>2</sub>CH<sub>2</sub>Ph, **3**), which can be isolated in 93% yield.

Scheme 3. Synthesis of 3.



+ 17 R - S - R + 42HCI + 84 HSR



**Figure 4.** Ball-and-stick diagram showing a) the  $[Cu_{16}(SR)_6Cl_{12}]^{2-}$  core, b) the full structure of **3**·1.5THF, including one  $[H(THF)_2]^+$  cation (hydrogen atoms, THF ligands, and THF solvate molecules omitted for clarity). Color legend: orange, Cu; yellow, S; green, Cl; red, O; gray, C.

Complex 3 crystallizes in the triclinic space group  $P\overline{1}$  as a THF solvate, 3.1.5THF (Figure 4). Like 2, complex 3 features a  $[Cu_{12}(SR'')_6]^{6+}$  "Atlas-sphere" core (Figure 4a). Within the core, the Cu–Cu distances range from 2.685(3) to 3.678(4) Å, while the average Cu–SR distance is 2.28 Å. These values are similar to those observed for 2. Each of the 12 Cu atoms in the  $[Cu_{12}(SR'')_6]^{6+}$  core is coordinated to one Cl<sup>-</sup> ligand. These Cl<sup>-</sup> ions are grouped into four groups of three. Each group of Clions forms a trigonal planar bonding pocket, which is filled with a Cu<sup>+</sup> ion. A thirteenth Cl<sup>-</sup> ligand (Cl13) is also bound to the  $[Cu_{12}(SR'')_6]^{6+}$  core, in an  $\mu_2$  interaction with Cu6 and Cu7. One of the outer  $Cu^+$  ions (Cu11) is bound by an R'SH ligand. while another (Cu5) is bound by a THF ligand. One of the "core" Cu atoms (Cu10) is also bound by a THF ligand. Additionally, complex 3 features a [Cu(HSR'')2] fragment appended to its outer surface via dative interactions with two Cl<sup>-</sup> ligands

(Cl12 and Cl13). It is likely that this peripheral fragment, along with the peripheral THF and R'SH ligands, is extremely labile. Not surprisingly, the <sup>1</sup>H NMR spectrum (*vide infra*) in THF-*ds* reveals a highly symmetric cluster, with only one magnetically unique thiolate ligand. Finally, the overall cluster charge is balanced by the presence of two  $[H(THF)_2]^+$  cations. While the H-bonded protons in these cations were not located in the difference Fourier map, their presence is supported by the close approach of two sets of THF molecules. Specifically, the distances between O3 and O4 (2.47(2) Å) and O8 and O8\* (2.36(1) Å) are similar to the O-O distances in other  $[H(THF)_2]^+$  and  $[H(Et_2O)_2]^+$  cations.<sup>42-49</sup>

The <sup>1</sup>H NMR spectrum of **3** in THF- $d_8$  reveals resonances at 3.47 and 3.37 ppm, assigned to CH<sub>2</sub> resonances of the six  $\mu_4$ -SCH<sub>2</sub>CH<sub>2</sub>Ph ligands. Likewise, resonances at 2.88 and 2.77 ppm are assigned to the CH<sub>2</sub> resonances of the thiol ligands. The

thiol SH proton resonance at 1.95 ppm is also present. A very broad resonance at 8.82 ppm is assigned to the O-H-O proton of the  $[H(THF)_2]^+$  counterion.<sup>45, 48-49</sup> For comparison, the O-H-O proton of the  $[H(THF)_2]^+$  counterion in  $[H(THF)_2][Al\{OC(CF_3)_3\}_4]$  is reported to appear at ca. 8 ppm.<sup>45</sup> The presence of thiolate and thiol environments in a 6:4 ratio, instead of the expected 6:3 ratio, suggests that a small amount of excess of thiol is present in the final product, which we have been unable to remove.

ESI-MS data were collected in negative ion mode for a THF solution of 3. The major feature of the spectrum at m/z =2129.8726 corresponds to the fragment [Cu<sub>15</sub>(SR'')<sub>6</sub>Cl<sub>10</sub>] (calcd m/z = 2129.8718) (Figure 5). Several other peaks are also observed. They are related to the parent ion by loss/gain of CuCl (m/z = 99). These data suggest that the  $[Cu_{12}(SR'')_6]^{6+}$  core of **3** is relatively stable, but that the outer  $Cl^{-}$  anions,  $Cu^{+}$  cations, and thiol ligands are more labile. Once again, we observed a signal only after addition of [NEt4][Cl] to the ESI-MS sample. A UV-vis spectrum of **3** in THF and features a broad absorption band at 355 nm (Figure S17), in good agreement with the spectrum observed for 2. The fluorescence spectrum of 3, recorded for the solid and excited at 365 nm, reveals a broad peak at 650 nm (Figure S20). We also briefly examined the chemical properties of complex 3. Similar to complex 2, it is insoluble in alkanes, Et<sub>2</sub>O, benzene, toluene, CH<sub>2</sub>Cl<sub>2</sub>, and MeCN. It is soluble in THF, although the cluster appears to partially decompose in that solvent upon standing at room temperature for 5 h, as evidenced by the deposition of a white powder and a bleaching of the yellow color. Complex 3 also reacts with pyridine to form 4, which was isolated in 95% yield after work-up.<sup>41</sup>



Figure 5. Partial ESI-MS of 3 in negative ion mode. Assignments:  $m/z = 2129.8726 [Cu_{15}(SR'')_6Cl_{10}]^-$  (calcd m/z = 2129.8718),  $m/z = 2527.6428 [Cu_{19}(SR'')_6Cl_{14}]^-$  (calcd m/z = 2129.8718),  $m/z = 2527.6428 [Cu_{19}(SR'')_6Cl_{14}]^-$ 

2527.4636),	m/z =	2431.7378	[Cu <sub>18</sub> (SR'	') <sub>6</sub> Cl <sub>13</sub> ] <sup>-</sup>	(calcd	m/z =
2431.5574),	m/z =	2327.6748	[Cu17(SR'	$^{\prime})_{6}Cl_{12}]^{-}$	(calcd	m/z =
2327.6667),	m/z =	2229.7747	[Cu16(SR'	')6Cl11]	(calcd	m/z =
2229.7683),	m/z =	2031.9645	[Cu <sub>14</sub> (SR'	')6Cl9]-	(calcd	m/z =
2031.9734),	m/z =	1932.0714	[Cu13(SR'	')6Cl8]-	(calcd	m/z =
1932.0750),	m/z =	1831.0859	[Cu <sub>12</sub> (SR'	')6Cl7]-	(calcd	m/z =
1831.1843).						

X-ray Absorption Spectroscopy Characterization. Previously, we demonstrated that X-ray absorption spectroscopy is a valuable tool for the structural characterization of copper nanoclusters.<sup>24, 26-27</sup> In particular, we showed that the XANES edge energy is highly sensitive to the average Cu oxidation state in Cu nanoclusters.<sup>24, 26-27</sup> Building on this past work, we measured the Cu K-edge XANES and EXAFS of nanoclusters 1 (synthesized using dibenzyl ether as the solvent), 2, and 3. The XANES spectra of nanoclusters 1, 2, and 3 feature edge positions at 8980.7, 8981.1, and 8980.5 eV (Figure S27), respectively. These values are essentially identical to those measured for the Cu(I) coordination complexes [CuCl(PPh<sub>3</sub>)]<sub>4</sub> (8080.9 eV) and CuCl (8981.9 eV),24,26 and corroborate our assignment of 1, 2, and 3 as Cu(I)-containing nanoclusters with no Cu(0) character. If 1, 2, and 3 did have some Cu(0) character, we would expect to observe edge positions at lower energies (comparable to 8979.6 eV for [Cu<sub>25</sub>H<sub>22</sub>(PPh<sub>3</sub>)<sub>12</sub>][Cl] or 8979.0 eV for Cu foil, for example).24, 26-27

The EXAFS spectra for nanoclusters 1, 2, and 3 show similar features (Table 1 and Figure 6). Specifically, there are two major peaks at ca. 1.8 and 2.3 Å in R-space. The first peak represents scattering from the light atoms (Cl and S) coordinated directly to Cu, while the second peak represents Cu-Cu scattering. Both features are more intense for 1, whose EXAFS also contains a prominent long-range path at ca. 3.8 Å. For all three nanoclusters, scattering involving nearest-neighbor Cu-Cl, Cu-S and Cu-Cu paths was simulated using the "Atlas-sphere" [Cu<sub>12</sub>(SR)<sub>6</sub>Cl<sub>12</sub>]<sup>6-</sup> core present in clusters 2 and 3. For the ligandbased paths, the expected coordination numbers are N(Cu-Cl) = 1.0 and N(Cu-S) = 0.5, which have nearly identical average distances of 2.27 and 2.28 Å, respectively. These similar pathlengths led us to combine the scattering paths for all ligands into a single Cu-L path in the EXAFS fit. The expected nearestneighbor coordination number N(Cu-Cu) is 2.0, at an average distance of 2.76 Å; however, there is a large range in the crystallographically-determined Cu-Cu distances (see above). To account for this variation, EXAFS data were fitted with two different Cu-Cu paths, following a previous successful approach.<sup>26-27</sup> The FEFF model<sup>50</sup> also predicts significant contributions from a variety of single-scattering paths at ca. 4.0 Å, which we modeled using a long Cu-Cu path.

**Table 1.** Comparison of average FEFF-predicted paths for the "Atlas-sphere" core  $[Cu_{12}(SR)_6Cl_{12}]^{6-}$ , with EXAFS curvefit parameters for nanoclusters **1**, **2**, and **3**.

Cluster	Path	Ν	R (Å)	$\frac{10^{3}}{(\text{\AA}^{2})}\sigma^{2}$
$[Cu_{12}(SR)_6Cl_{12}]^{6-}$	Cu-L1	1.5	2.278	n.a.
	Cu-Cu1	1.33	2.718	
	Cu-Cu2	0.67	2.944	
	Cu-Cu3	2.87	4.03	
1 <sup>a</sup>	Cu-L	1.8(3)	2.249(6)	3.9(3)

	Cu-Cu1	1.6(3)	2.796(9)	$4.6(2)^{b}$		
	Cu-Cu2	0.4(2)	2.983(9)	$4.6(2)^{b}$		
	Cu-Cu3	2.4(4)	4.047(2)	8.9(5)		
<b>2</b> °	Cu-L	1.2(2)	2.240(2)	3.0(9)		
	Cu-Cu1	1.5(4)	2.77(4)	$11(4)^{d}$		
	Cu-Cu2	0.4(2)	2.982(1)	$11(4)^{d}$		
<b>3</b> °	Cu-L	1.5(3)	2.298(6)	4.1(3)		
	Cu-Cu1	1.6(5)	2.71(1)	12(4) <sup>f</sup>		
	Cu-Cu2	0.7(3)	2.92(2)	12(4) <sup>f</sup>		
$A^{a} N_{1} = 23  AR = 1.0 - 4.5  \text{Å}  Ak = 3.0 - 13.5  \text{Å}^{-1}  AE_{0} = 5.7(5)$						

<sup>a</sup>  $N_{idp} = 23$ ,  $\Delta R = 1.0 - 4.5$  Å,  $\Delta k = 3.0 - 13.5$  Å<sup>-1</sup>,  $\Delta E_0 = 5.7(5)$ . <sup>b</sup> Constrained to the same value.  ${}^{\circ}N_{idp} = 15$ ,  $\Delta R = 1.0 - 3.0$  Å,  $\Delta k = 3.0 - 14.5$  Å<sup>-1</sup>,  $\Delta E_0 = 5.7(2)$ . <sup>d</sup> Constrained to the same value. <sup>e</sup>  $N_{idp} = 13$ ,  $\Delta R = 1.0 - 3.0$  Å,  $\Delta k = 3.0 - 13.3$  Å<sup>-1</sup>,  $\Delta E_0 = 4.7(5)$ . <sup>f</sup> Constrained to the same value. In all fits, the value of  $S_0^2$  was fixed at 0.8, in accordance with our previous analyses of Cu(I) standards and Cu-based clusters,<sup>26-27</sup> and  $\Delta E_0$  was refined as a global fit parameter. Uncertainties are shown in parentheses; values without uncertainties were fixed during curvefitting.

Satisfactory fits were achieved for all three nanoclusters. For example, for nanocluster 2, the curve fit gives a Cu-L pathlength of 2.240(2) Å (N = 1.2(2)), and the combined value of N(Cu-Cu) is 1.9(6). These parameters are in good agreement with the FEFF-predicted paths for the "Atlas-sphere" core, [Cu12(SR)6Cl12]6-. A similarly good fit was achieved for nanocluster 3. For nanocluster 1, the curve fit gives a Cu-L pathlength of 2.246(6) Å (N = 1.8(3)), while the combined value of N(Cu-Cu) is 2.0(5). Most significantly, these parameters agree well with those determined for 2 and 3, and demonstrate that a single "Atlas-sphere" structural model can be used to describe the EXAFS of all three nanoclusters, albeit with slight differences in EXAFS intensity (which likely arises from perturbations of the core due to the different outer surface environments). These findings further reinforcement our hypothesis that nanocluster 1 is an "Atlas-sphere"-type cluster, and not a low-valent, Cu(0)-containing nanocluster as originally surmised.

For further comparison, we also recorded EXAFS data for an authentic Cu<sub>14</sub> cluster, [Cu<sub>14</sub>H<sub>12</sub>(phen)<sub>6</sub>(PPh<sub>3</sub>)<sub>4</sub>][Cl]<sub>2</sub>, which we synthesized and structurally characterized in 2015.<sup>51</sup> In the solid state, [Cu<sub>14</sub>H<sub>12</sub>(phen)<sub>6</sub>(PPh<sub>3</sub>)<sub>4</sub>][Cl]<sub>2</sub> features a significantly shorter average Cu-Cu distance than is found in either 2 or 3, making it a reasonable model for the Cu<sub>14</sub>(SR)<sub>10</sub> structure proposed by Zhang and co-workers. Its EXAFS spectrum contains a broad signal with multiple, overlapping components centered at ca. 2 Å (Figure 6a). The fit was conducted using contributions from Cu-L (L = N, P) scattering, as well as three distinct Cu-Cu single-scattering paths (Table S4). In particular, the curve fit gives Cu-N and Cu-P pathlengths of 2.07(1) and 2.30(1) Å, respectively, while the combined value of N(Cu-Cu) is 4.1(5). These parameters are in good agreement with those extracted from the X-ray crystallographic analysis. More importantly, though, the N-weighted average Cu-Cu EXAFS pathlength is 2.60 Å, which is close to the value of 2.55 Å found for bulk Cu metal,<sup>24</sup> and much different from the Cu-Cu pathlengths measured for nanocluster 1. Finally, the prominent feature at ca. 4 Å in the EXAFS of [Cu<sub>14</sub>H<sub>12</sub>(phen)<sub>6</sub>(PPh<sub>3</sub>)<sub>4</sub>][Cl]<sub>2</sub> is reproduced well by a near-collinear multiple-scattering path (Cu-Cu-Cu, N

= 6,  $\angle$  160.1°). Overall, the spectrum of Cu<sub>14</sub> exemplifies the EXAFS expected for a Cu<sub>14</sub> nanocluster with strong Cu-Cu bonding, and is very different from the EXAFS of 1, 2, and 3, supporting our conclusion about the structure of 1.

Comparison to Other Reported Copper Thiolate Nanoclusters. As mentioned in the Introduction, several thiolate-protected Cu APNCs with partial Cu(0) character have been reported in the past few years, including [Cu15(GSH)4], [Cu<sub>9</sub>(SC<sub>6</sub>H<sub>4</sub>-*p*-F)<sub>7</sub>], and [Cu<sub>9</sub>(SC<sub>6</sub>H<sub>4</sub>-*p*-Br)<sub>6</sub>].<sup>15, 17</sup> Many of these low-valent nanoclusters were reportedly formed by direct reaction of a Cu(II) salt with an alkyl or aryl thiol, which acts as both reducing agent and capping ligand. On the basis of the reactivity we report here, we now believe that these previous reactions do not result in the formation of low-valent Cu AP-NCs. Instead, we suspect that they lead to formation of Cu(I)containing thiolate clusters, similar in formulation and structure to complexes 1, 2, and 3. Given the apparent thermodynamic stability of the "Atlas-sphere" structure type, as revealed by the structures of 2 and 3, as well as the structures of  $[Cu_{12}(SR)_{6}X_{12}][CuX]$  (X = Cl, Br; R = CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>), [Cu12(SR)6Cl12][CuCl]5, [Cu12(SMe)6(CN)6], and [Cu12E6L8] (E = S, Se; L = phosphine),<sup>37-38, 52-55</sup> it is likely that many of these complexes also feature a [Cu12(SR)6]6+ core. That being said, other core structures are also possible, including [Cu4(SR)4] (R = 2,6-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4,6-<sup>i</sup>Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>),  ${}^{56-57}$  [Cu<sub>4</sub>(SR)<sub>6</sub>]<sup>2-</sup>(R = Me, Et, <sup>i</sup>Pr, Ph, *p*-Cl-C<sub>6</sub>H<sub>4</sub>,  $o^{-t}Bu$ -C<sub>6</sub>H<sub>4</sub>), <sup>58-65</sup> [Cu<sub>5</sub>(SR)<sub>6</sub>]<sup>-</sup> (R = <sup>t</sup>Bu, 2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>, 1-adamantyl),<sup>64, 66-68</sup>  $[Cu_5(SR)_7]^{2-}$  (R = Me, Ph),<sup>62, 69-70</sup> [Cu<sub>6</sub>(SR)<sub>6</sub>( $\mu_6$ -Br)] (R = 1-(thiolato)triptycene),<sup>71</sup>  $[Cu_8(SR)_8]$  (R = 2,4,6-iPr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>),<sup>57, 72</sup>  $[Cu_8(SR)_6Cl_6]^{2+}$  (R =  $CH_2CH_2NH_3$ ),<sup>55</sup> and  $[Cu_{12}(SR)_{12}]$  (R = 2-(Me\_3Si)C\_6H\_4).<sup>73</sup>



**Figure 6.** Comparison of Cu K-edge EXAFS for (a)  $[Cu_{14}H_{12}(phen)_6(PPh_3)_4][Cl]_2$  and **1**; and (b) **2** and **3**. All spectra are shown as FT magnitudes in non-phase corrected *R*-space (points). Parameters for the curvefits (solid lines) are shown in Tables 1 and S4. Spectra are offset vertically for clarity.

The reactivity of Cu(I) and Cu(II) salts with thiols and thiolates is actually well explored.<sup>74</sup> Despite this long history, there is no crystallographically authenticated example of this reaction resulting in formation of a Cu(0)-containing product. For example, Kroneck and co-workers monitored the reaction of [Cu(MeCN)<sub>4</sub>][ClO<sub>4</sub>] with a variety of thiols in MeCN/H<sub>2</sub>O. These reactions produce thiolate-containing Cu(I) coordination polymers exclusively.75 In no case did they observe reduction of Cu(I) to Cu(0). Similarly, reaction of [Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>] with HSC<sub>6</sub>H<sub>4</sub>-o-SiMe<sub>3</sub> results in formation of the Cu(I) nanocluster, [Cu(SC<sub>6</sub>H<sub>4</sub>-o-SiMe<sub>3</sub>)]<sub>12</sub>.<sup>73</sup> More recently, Donahue and co-workers found that reaction of CuCl with [n-Bu<sub>4</sub>N][Cl] and NaSR (R = 1-(thiolato)triptycene) results in formation of the monometallic Cu(I) "ate" complex, [Cu(SR)<sub>2</sub>]<sup>-,71</sup> It is also useful to survey the reactivity of Ag and Au salts with thiols. For instance, reaction of AgNO3 with RSH/NEt3 in MeCN resulted in formation of [Ag(SR)]<sup>n</sup> oligomers.<sup>76-77</sup> The reaction conditions are similar to those used in our study, yet no reduction to Ag(0) was observed, despite the fact that Ag(I) is a much stronger oxidant than Cu(I).78 Similarly, reaction of AgNO3

with PhSH/[NMe4][Cl] in MeOH/MeCN yields a series of Ag<sup>I</sup>(SPh) "ate" complexes.<sup>79</sup> Again, no reduction to Ag(0) is observed. With respect to Au(I), which is a stronger oxidant than either Ag(I) or Cu(I),<sup>78</sup> reaction of H[AuCl4] with excess RSH in water results in formation of [Au<sup>I</sup>(SR)]<sub>n</sub> in excellent yields,<sup>80</sup> although in this case, reduction to metallic gold can be observed if the reaction mixture gets too hot. Similarly, reaction of Na[AuCl4] with 3 equiv of RSH in EtOH also results in formation of [Au<sup>I</sup>(SR)]<sub>n</sub>.<sup>81</sup> This procedure is compatible with a wide variety of R groups, including "Bu and C<sub>12H25</sub> (which were employed in the current study).

The well-known photochemical properties of Cu(I) clusters further buttresses our argument that the material isolated by Zhang and co-workers is a Cu(I)-containing "Atlas-sphere" nanocluster, and not the mixed valent nanocluster, Cu<sub>14</sub>(SR)<sub>10</sub>, that was original proposed. For example, the "Atlas-sphere" clusters, [Cu<sub>12</sub>E<sub>6</sub>L<sub>8</sub>] (E = S, Se; L = phosphine), are strongly luminescent, with measured PL quantum yields of up to 90%.<sup>52-<sup>54</sup> In fact, many Cu(I)-containing clusters are known to be photoluminescent,<sup>13, 82-89</sup> including many Cu(I)-thiolate and Cu(I)thiolate/halide clusters.<sup>13, 83, 87-89</sup> For example, [Cu(SR)]<sub>n</sub> (n = 2, 4, 7; R = p-S-C<sub>6</sub>H<sub>4</sub>-NMe<sub>2</sub>)<sup>13</sup> features an emission peak between 480 and 560 nm, depending on its nuclearity, while [(Cu(S'Bu))<sub>4</sub>(dppe)]<sub>n</sub> (dppe = bis(diphenylphosphino)ethane) and [(CuS'Bu)<sub>6</sub>(bix)]<sub>n</sub> (bix = 1,4-bis(imidazole-1-ylmethyl)benzene) emit at 603 and 629 nm, respectively.<sup>88</sup></sup>

## Conclusion

We have examined the reactions of CuCl<sub>2</sub> with a variety of thiols (RSH) under anhydrous conditions. In the cases where R = n-Bu and R = CH<sub>2</sub>CH<sub>2</sub>Ph, we isolated "Atlas-sphere"-type nanoclusters in good yields. Both nanoclusters are built around identical [Cu12(SR)6]<sup>6+</sup> core structures and both contain Cu(I) ions exclusively. Neither cluster features any Cu(0) character. In the case where  $R = n-C_{12}H_{25}$ , we generated an insoluble Cu(I)-containing thiolate nanocluster. The insolubility of this material prevented us from growing X-ray quality crystals. However, we believe this cluster also features an "Atlassphere" core on the basis of a comparative XANES and EXAFS analysis. Our conclusion concerning the nature of this material is further strengthened by our XPS characterization data, as well as the observation that the "Atlas-sphere" structure type is a conserved across a variety of thiolate ligands. Contrary to previous reports, we do not believe that this material is a mixed valent, Cu(0)-containing nanocluster.

Our conclusions concerning the nature of this material are also better aligned with previously reported group 11 thiolate chemistry, which has been extensively studied. In particular, this past work suggests that the M(0) state is not accessible without addition of stronger reducing agents, such as NaBH4. To the best of our knowledge, all previously reported reactions of Cu(II) salts with thiols have resulted only in formation of Cu(I)-containing products. Stated differently, thiols alone cannot reduce  $Cu^{2+}$  or  $Cu^{+}$  to Cu(0). Perhaps most importantly, it is apparent that the synthesis of thiolate-stabilized, Cu(0)-containing APNCs is an unsolved synthetic problem. Their isolation would represent an important synthetic advance, but these materials remain elusive, in contrast with the plethora of known thiolate-stabilized Au(0)- and Ag(0)-containing APNCs. Going forward, we will continue to pursue the synthesis of Cu(0)-containing, thiolate-stabilized APNCs. However, their successful

isolation will likely require the development of new ligands and new synthetic procedures.

# ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

X-ray data for compound 2 and 3.1.5THF (CIF)

Experimental procedures, crystallographic details, and spectral data (PDF)

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#### Notes

The authors declare no competing financial interest.

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Fluorescent, "Atlas-sphere"-type copper(I)-containing nanoclusters were prepared by reaction of  $CuCl_2$  with a variety of thiols. In contrast to past reports, we find no evidence for reduction to Cu(0) under the reaction conditions.