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Exposing the delocalized Cu-S π bonds on Au₂₄Cu₆(SPh*t*Bu)₂₂ nanocluster and its application in ring opening reaction

Jinsong Chai,⁺ Sha Yang,⁺ Ying Lv, Hanbao Chong, Haizhu Yu,* and Manzhou Zhu*

Abstract: Bimetallic nanomaterials are of major importance in catalysis. In this study, we synthesized a novel Au-Cu bimetallic nanocluster and found it effective to catalyze the epoxide ring opening reaction. The catalyst was analyzed by SCXRD and ESI-MS to be Au₂₄Cu₆(SPhtBu)₂₂ (Au₂₄Cu₆ for short). Six copper atoms were found to exclusively occupy the surface positions in two groups with three atoms for each, and each group was bonded with three thiolate ligands to give a planar motif reminiscent of a benzene ring. In the epoxide ring opening reaction, Au₂₄Cu₆ exhibited superior catalytic activity compared to other homometallic and Au-Cu alloy NCs, such as Au_{25} and $Au_{38\text{-}x}Cu_x$. Control experiments and density functional theory (DFT) calculations revealed that the π conjugation among the Cu-S bonds played a pivotal role. This study demonstrates a unique π conjugation established among the Cu-S bonds as a critical structural motif in the nanocluster, which facilitates the catalysis of a novel type of ring opening reaction.

Owing to the high surface area and unique properties, metal nanoparticles have emerged as an important category of heterogeneous catalysts for a wide range of chemical transformations.^{1,2} Recent studies have shown that catalytic activity can be enhanced via tuning the composition, size, shape, and surface structure of the nanoparticles.³⁻⁵ However, a detailed, mechanistic explanation of the catalytic performance of nanoparticles is still lacking, in part due to the mysterious nature of the surface layer of the catalyst. Ultrasmall metal nanoclusters (size < 2 nm), which have excellent stability, molecular-like spectroscopic properties, well-defined atomic packing modes, and are amenable to characterization by single crystal X-ray diffraction (SCXRD) techniques, have emerged as a means of studying catalytic mechanisms and thereby improving catalytic activity.⁶⁻¹¹

To date, a variety of metal nanoclusters have been found to exhibit excellent catalytic performance in oxidation, hydrogenation, and carbon-carbon coupling reactions.12-15 Specifically, the electronic structure of nanoclusters, which is amenable to modeling by theoretical calculations,¹⁶⁻¹⁸ greatly influences their catalytic activities. In this context, both precise elucidation of the catalytic mechanism and the rational modifications to the electronic structure of the nanocluster catalyst become possible. For example, Pt₁Au₂₄(SC₆H₁₃)₁₈ and Au₁₁(PPh₂Py)₇Br₃ nanoclusters show higher activity than the in hydrogen traditional catalysts production and nitrobenzaldehyde hydrogenation. Based on the structures of

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nanoclusters, the mechanisms for both reactions were successfully elucidated.^{19,20} Tsukuda et al. improved the performance of an Au_{25} catalyst for the aerobic oxidation of benzyl alcohol by doping it with Pd, a change ascribed to electron transfer from Pd to Au in the Pd_1Au_{24} cluster.²¹ These successes greatly intrigued us, and we wondered whether the scope of nanocluster catalysis could be broadened further.

The introduction (doping) of a foreign metal (e.g. Ag, Cu, Pt, Pd, etc.) atom(s) to gold nanoclusters has been shown to perturb their electronic structure.²²⁻²⁷ Zheng et al. found that Cu atoms present multiple coordination with ligands, and preferentially locate on the nanocluster surface.^{28,29} Similar observations were observed in a series of Au-Cu alloy nanoclusters, reported by our group.³⁰⁻³¹ In a continuation of these studies, we use the gold and copper salts to prepare new Au-Cu alloy nanoclusters that bear catalytically active Cu atoms on the surface. This could give rise to peripheral Cu-ligand motifs, which are expected to facilitate novel catalytic reactions.

Herein, a new Au-Cu bimetallic NC, i.e. $Au_{24}Cu_6(SPhtBu)_{22}$ is synthesized, crystallized, and characterized by SCXRD. The structure of $Au_{24}Cu_6(SPhtBu)_{22}$ comprises a 30-atom metal core (24 gold atoms and 6 copper atoms), which is protected by 22 thiolate ligands. The 6 copper atoms are doped onto the surface of the alloy nanocluster and exist in two groups, and each group is bonded to three thiolate ligands to form a planar, trimeric $Cu_3(SR)_3$ structure that resembles a phenyl group. The exposure of the planar $Cu_3(SR)_3$ motif is pivotal to the catalytic activity of $Au_{24}Cu_6$ in the epoxide ring opening reaction. Theoretical calculations have identified the active site to be the planar $Cu_3(SR)_3$ and demonstrated that Cu(d)-S(p) π -bonding and the conjugation between different π -moieties are mainly responsible for the catalytic activity.

The Au₂₄Cu₆(SPh*t*Bu)₂₂ alloy cluster was prepared by an *in situ* two-phase ligand exchange method.³⁰ CuCl₂ and reduced glutathione were dissolved in water. Then, an aqueous solution of HAuCl₄·4H₂O was added and the mixture was stirred. After 20 mins, a solution of borane-tert-butylamine complex and 4-tert-butylbenzenethiol in toluene was added quickly. After 4 hours, the crude product (in toluene) was washed several times with methanol and collected by centrifugation to give a pure product (yield: 5% based on Au atom) (Figure S1a). The product shows two main peaks at 380 and 550 nm in UV-Vis (Figure S2).

Crystals were obtained by layering methanol onto a CH₂Cl₂ solution of the cluster, with a yield of ~1% based on the initial Au atom (Figure S1b). SCXRD measurements determined its formula to be Au₂₄Cu₆(SPhtBu)₂₂. The Au₂₄Cu₆ NC crystallizes in a triclinic crystal system (space group P-1). The details of crystal data and the refinement are provided in the Supporting Information.

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Figure 1. The core (a), surface motif (b) and hexagons (c) of the $Au_{24}Cu_6$ alloy nanocluster (color labels: magenta/light green = Au, orange = Cu, cyan = S; C and H atoms are not shown).

The structure of Au₂₄Cu₆(SPhtBu)₂₂ (Figure S3a) is distinct from the Au₃₀(S-Adm)₁₈ and Au₃₀S(StBu)₁₈ nanoclusters, albeit all of them contain the same number of metal atoms.32,33 Au₂₄Cu₆ consists of a 30-atom metal core (24 gold and 6 copper atoms), with 22 peripheral thiolate ligands. As shown in Figure S3b, each unit cell of this NC contains a pair of enantiomers (for clarity, only one of them is depicted in Figure S3b). Interestingly, all six Cu atoms are doped onto the staple motifs, and therefore the structure of the NC could be viewed as comprising an Au₁₈ kernel flanked by a pair of Au₃Cu₃S₉ staple motifs on each side and four bridging thiolate ligands (Figure S3b). In detail, the Au₁₈ kernel is composed of one Au₁₃ unit (Figure 1a, top left) and one Au₁₁ unit (top right), that share six Au atoms (pale blue spheres). In each $Au_3Cu_3S_9$ motif (Figure 1b), the Cu atoms are all triply coordinated to the S atoms. However, the three Cu atoms in each motif are also cyclically bonded to three S ligands to form a planar Cu₃(SR)₃ structure that closely resembles a phenyl group (Figure 1c). The structure of the two Cu₃(SR)₃ motifs are almost the same (Figure S4). For clarity, we take the left Cu₃(SR)₃ motif as an example for a detailed analysis. The bond lengths of Cu-S are in the range of 2.188-2.374 Å. The trimeric ring motif adopts a planar conformation, and the S-Cu-S angles are 103.54°, 115.20° and 116.38°, respectively. The angle sum of the hexagon ring is 716.55°.

The planar Cu₃(SR)₃ structure as a component on the surface of nanoclusters is unprecedented and intriguing. We used DFT calculations to explore the electronic structure of Au₂₄Cu₆ with such a unique type of surface motif. The optimized geometry of Au₂₄Cu₆ showed the Cu₃(SR)₃ motif to be planar, which is consistent with the SCXRD analysis. In addition, the Cu(d)-S(p) π -bonding and anti-bonding interactions were found to significantly contribute to the molecular orbitals. Particularly, the π -bonding and the conjugation between different π -moieties within the planar Cu₃(SR)₃ structure can be seen clearly in several highest occupied molecular orbitals such as HOMO-15, HOMO-16, and HOMO-18. Figure 2 shows an illustrative figure on the conjugation between different π -orbitals in one Cu₃S₃ structure, and the full details are given in Figure S5.



Figure 2. Schematic diagrams of the $\pi\mbox{-bonding}$ of selected HOMOs of $Au_{24}Cu_6$ nanocluster.

Electrospray ionization mass spectrometry (ESI-MS), thermal gravimetric analysis (TGA), nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) were used to confirm the formula of the $Au_{24}Cu_6$ nanocluster, and the details are given in Figures S6-S12.

We used the epoxide ring opening reaction as a model reaction to investigate the catalytic activity of the Au₂₄Cu₆. After the optimization of catalytic conditions (Figure S13-S14), the catalytic activity of the Au24Cu6 was tested. For comparison, the capacity of other nanoclusters (including the popular Au25,34 and the alloy Au_{38-x}Cu_x³¹ and Ag₂₈Cu₁₂³⁵ nanoclusters) were also tested for the same reaction. NMR analysis was used to analyze the product (Figure S15-S16). Detailed results are given in Table 1. In the absence of a catalyst (entry 1), a yield of 3% was achieved after ~12 hours. The Au-SPhtBu complex (Figure S17) exhibited a low catalytic activity (entry 2), and the yield is similar to that of the blank reaction. To our delight, the Au₂₄Cu₆ NC (single crystal) showed remarkable activity, yielding conversion of 96% after 12 hours (Table 1, entry 4 and Figure S18), similar to the SBA-15 (Table 1, entry 9). In contrast, Au₂₅ showed quite poor catalytic activity (4% conversion, entry 3). This result indicates that Au atoms are unlikely to be the active site of Au₂₄Cu₆. The conversion was also very low (3%) when another Au-Cu alloy cluster, Au_{38-x}Cu_x, was tested under the same conditions. This suggests that the specific structural motifs, rather than the general electron transfer between the Cu and Au atoms, account for the significantly higher catalytic activity of Au₂₄Cu₆. Interestingly, another Ag-Cu alloy Ag₂₈Cu₁₂, which bears similar Cu₃S₃ cyclic motifs to Au₂₄Cu₆(SPhtBu)₂₂ but in a chair-like configuration, showed poor catalytic activity (entry 6, 7% conversion). In addition, the Cu₃(SR)₃(¹Pr₃P)₃ complex³⁶ (Cu₃(SR)₃(Pr₃P)₃ complex was characterized by ESI-MS and TGA shown in Figure S19) also showed a lower catalytic activity (Table 1, entry 10). Taking the results together, we conclude that the planar nature of the Cu_3S_3 motifs is essential for effective catalysis and the superior catalytic activity of Au24Cu6 was suggested to originate from the synergy between gold and copper atoms.

Recycling tests of the $Au_{24}Cu_6$ catalyst showed that the catalytic activity maintained after three cycles (entries 7 and 8).

The UV-vis absorption and ESI-MS spectra of $Au_{24}Cu_6$ alloy recorded before and after the catalysis proved it to be stable under the reaction conditions (Figure S20).

 Table 1. Epoxide ring opening reaction under different catalysts.^[a]



The $Au_{24}Cu_6$ was further examined for epoxide ring opening reaction of various epoxide derivatives and alcohols (Table S1). This nanocluster indeed shows high catalytic activity for the epoxide ring opening.

To investigate the catalytic mechanism of Au₂₄Cu₆, we carried out DFT calculations. It was found that the planar Cu₃S₃ motif is the active site. The left and the right Cu₃S₃ motifs were found to show comparable reactivity (Figure S21), and thus only the energy profiles of the left Cu₃S₃ motif were given in Figure 3 for clarity reasons. The DFT calculations indicate that the approach of the substrate to the Au atom is significantly more energydemanding (Figure S22). Also, epoxide is preferentially activated compared to MeOH (Figure S23). As shown in Figure 3, the activation of the epoxide could occur via two modes (Prec1 and Prec2), both of which result in ²C-O bond dissociation. In Prec1, only one Cu atom participates in the ²C-O activation, and the formed O-Cu bond slightly distorts the planarity of the Cu₃S₃ motif. In contrast, two Cu atoms participate in the activation process in Prec2, and the formed O-Cu and ²C-Cu bonds significantly distort the planar Cu₃S₃ structure into a chair-like one. The relative energy of Prec2 is higher than that of Prec1 by 0.3 eV, even though the ²C atom is stabilized by coordination with the Cu atom. This phenomenon is attributed to the perturbation of the π -interactions in **Prec2** and is disfavored. From Prec1, the energy of the reaction system decreases with the approaching of MeOH until the formation of the intermediate **Tss-1**. After that, the C-O bond gradually forms to generate the transition state **Tss-2**, in which the C-O bond is shortened to 2.37 Å (from 3.43 Å in **Tss-1**). The further approach of the MeOH results in an automatic H transfer from the hydroxyl group of MeOH to the O atom of epoxide, and the energy decreases continuously throughout this process. Finally, the release of the product (**Tss-3** \rightarrow **Prod**) is thermodynamically favored by 1.2 eV, with simultaneous regeneration of the catalyst Au₂₄Cu₆.

From Figure 3, the Au₂₄Cu₆ catalyzed epoxide ring opening reaction occurs via the C-O bond cleavage of styrene oxide, successive C(epoxide)-O(alcohol) bond formation and H-transfer, and the final catalyst regeneration steps. The second step is the rate-determining step, and the overall energy demand is 1.07 eV which is achievable under the experimental condition (60 °C). In addition, according to Mulliken charge analysis (Table S2), the Cu₃S₃ motif actually acts as the electron donor, transferring an electron to the epoxide substrate to activate its C-O bond. Although other nanoclusters such as Ag₂₈Cu₁₂ also has Cu₃S₃ motif but in a chair-like configuration. The DFT result shows that using the Ag₂₈Cu₁₂ as the catalyst, the relative energy is higher than that of Au₂₄Cu₆ by 0.65 eV (Figure S21). Therefore, Au₂₄Cu₆ NC with the planar nature of the Cu₃S₃ motifs exhibited superior catalytic activity compared to other NCs.



Figure 3. Energy profile for Au₂₄Cu₆ catalyzed epoxide ring opening reaction.

In summary, a novel Au-Cu bimetallic nanocluster Au₂₄Cu₆(SPh*t*Bu)₂₂ is obtained, and the cluster is found to catalyze the epoxide ring opening reaction, which is the first report of a nanocluster catalyst for this reaction. The composition and atomic structure of Au₂₄Cu₆(SPh*t*Bu)₂₂ were verified by a variety of characterization techniques, including SCXRD, ESI-MS, TGA, and XPS. All six copper atoms are present on the surface of the alloy nanocluster as two phenyl-like Cu₃(SR)₃ structures. DFT calculations demonstrated that the Cu₃(SR)₃ structure, the Cu(d)-S(p) π -bonding, and the conjugation between different π -moieties in Au₂₄Cu₆(SPh*t*Bu)₂₂ are all essential for catalysis. One Cu atom acts as the active site to promote C(benzyl)-O bond dissociation. Subsequently, the approach of MeOH results in the formation of a C(alcohol)-O(epoxide) bond, associated with an automatic H transfer from

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the alcohol to the epoxide moiety. Finally, the release of the ring opening product and the catalyst regeneration occur easily. This study gives new insights into the electronic characteristics of alloy nanoclusters and invites studies into their rational design.

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Keywords: $Au_{24}Cu_6 \cdot \pi$ -bonding \cdot ring opening reaction \cdot catalyst

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