Comproportionation Synthesis of Copper(I) Alkynyl Complexes Encapsulating Polyoxomolybdate Templates: Bowl-Shaped Cu_{33} and Peanut-Shaped Cu_{62} Nanoclusters

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S *Supporting Information*

ABSTRACT: Comproportionation reaction of Cu(II) salt and copper metallic powder in the presence of *tert*-butylacetylene ($tBuC{\equiv}CH$) in methanol at room temperature yielded discrete Cu(I) *tert*-butylethynide clusters whose identity depended on the particular co-existing anion employed. Introduction of polyoxomolybdate to the reaction system afforded two new core–shell nanoclusters, $[Cu_{33}(tBuC{\equiv}C)_{24}(Mo_4O_{16})]{\cdot}BF_4$ (**3**) and $[Cu_{62}(tBuC{\equiv}C)_{34}(Mo_5O_{19})_2(MoO_4)_2(OTf)_2(OH)_4]{\cdot}(OTf)_2$ (**4**). Complexes **3** and **4** represent the first examples of high-nuclearity Cu(I) clusters that encapsulate polyoxometalate templates, and the latter features the largest Cu(I) alkynyl cluster known to date. The present study not only demonstrates a new paradigm for the designed synthesis of Cu(I) alkynyl clusters but also opens the door to understanding Cu(I) alkynyl structural chemistry.

The construction of high-nuclearity ligand-protected metal nanoclusters has long intrigued synthetic chemists as a fascinating research endeavor.[1] The main challenge within this field is that synthetic design involving optimal matching of the inherent bonding capacity of metal and ligand components is often achievable via intuition or trial-and-error. In this context, despite considerable recent advances in the assembly and structure determination of Ag(I) alkynyl and chalcogen-stabilized Cu(I) and Ag(I) nanoclusters,[2] facile synthesis of comparable Cu(I) alkynyl clusters remains elusive. As the +1 oxidation state of copper is susceptible to be oxidized to the much more stable and soluble +2 state, there are very few stable Cu(I) salts that are soluble in common solvents that can be used as synthetic precursors. Furthermore, Cu(I) alkynyl systems have a natural propensity to aggregate indiscriminately to form intractable polymeric materials, which makes the isolation of discrete clusters more challenging.[3] Accordingly, only several high-nuclearity Cu(I) alkynyl clusters have been reported to date. Tasker et al. synthesized a series of clusters of the type $[Cu_{x+y}(hfac)_x(C{\equiv}CR)_y]$ ($hfac^-$ = hexafluoropentane-dionate; R = Pr, Bu, *n*-pentyl, *n*-hexyl) from the reaction of Cu_2O, hfacH and respective alkynes in *n*-hexane under anaerobic and anhydrous conditions.[4] In their reports, the significant role of $hfac^-$ as a "capping ligand" to prevent infinite aggregation and stabilize the cluster periphery was highlighted, yielding the largest Cu(I) alkynyl aggregate with a nuclearity of 26 for R = *n*-pentyl.[4a]

Along different paths, Weiss and Che et al. prepared the homoleptic $[tBuC{\equiv}CCu]_x$ complex, which was recrystallized from *n*-hexane and benzene as a Cu_{24} and Cu_{20} oligomer, respectively.[5] More recently Zhu et al. reacted $Cu(OAc)_2$ with $tBuC{\equiv}CH$ in methanol to generate a tetradecanuclear cluster $[Cu_{14}(tBuC{\equiv}C)_{10}(OAc)_4]$.[6] These two findings, in contrast to that of Tasker et al., highlight the $tBuC{\equiv}CCu$ system as a notable exception that favors formation of discrete entities without a "capping ligand". Presumably, formation of these clusters can be rationalized on the basis of the intrinsic properties of the $tBuC{\equiv}C^-$ ligand, which is considerably more electron-donating and sterically bulky as compared with other congeners to stabilize a cluster structure.[7] Pursuing this clue, we focused on assembly of high-nuclearity Cu(I) clusters with $tBuC{\equiv}CH$. The next step is to seek a simple and effective synthetic route to attain this goal.

It is well known that in copper-catalyzed alkyne–azide cycloaddition (CuAAC) reactions, a common approach to catalyst generation involves the use of a Cu(II) salt and copper metallic powder to generate Cu(I) in situ, and Cu(I) alkynide complexes have been proven to be key intermediates.[8] Evidently the affinity between Cu(I) and alkynide ligand provides an important driving force behind the comproportio-nation reaction.[6,9] We therefore anticipated that performing the comproportionation reaction in the absence of an azide could result in the formation of isolable Cu(I) alkynyl clusters.

Gratifyingly, our attempt to adopt the comproportionation methodology has led to success: reaction of CuX_2 (X = BF_4^- (**1**), OTf^- (**2**)) and copper metallic powder in the presence of $tBuC{\equiv}CH$ in methanol at room temperature provided $[Cu_{17}(tBuC{\equiv}C)_{16}(MeOH)](BF_4)$ (**1**) and $[Cu_{18}(tBuC{\equiv}C)_{16}(H_2O)_2](OTf)_2{\cdot}2MeOH$ (**2**) in high yields. Both complexes crystallize as discrete cation–anion pairs, and in either cationic cluster the sterically bulky $tBuC{\equiv}C^-$ ligands cover the surface of the assembled Cu(I) kernel except for small clefts filled by solvated molecules, accounting for the cluster stability (see synthetic details, crystal data, and structure description in Supporting Information). Furthermore, hydrophobic interactions between the cationic clusters suppress their free rotation in the crystal lattice, which is also important for single crystal formation.[10] With the structures at hand, we gained a better understanding of the unique ability of $tBuC{\equiv}C^-$ to produce

tractable, discrete cluster entities. It is seen that both BF_4^- and OTf^- affect the nuclearity of the cationic clusters, showcasing the significance of the co-existing counteranion in phase formation.[11] It should be mentioned that effective compro-portionation can be achieved under mild and open-air conditions,[12] making it a facile, convenient protocol that constitutes an important addition to the toolbox of synthesizing discrete Cu(I) alkynyl complexes.

The ease of the $tBuC\equiv CCu$ system to form discrete polynuclear aggregates made us envision that judicious introduction of anionic templates into the reaction system may further facilitate the aggregation of Cu(I) centers to afford large clusters; moreover, based on the observation that the self-assembly of **3** and **4** is anion dependent, we also expected to observe the same phenomenon in the large assemblies. As the first investigation of anion templation in Cu(I) alkynyl chemistry, we report herein a surprisingly facile approach that takes advantage of the templating effect of polyoxomolyb-dates,[13] yielding two nanoclusters, $[Cu_{33}(tBuC\equiv C)_{24}(Mo_4O_{16})]\cdot BF_4$ (**3**) and $[Cu_{62}(tBuC\equiv C)_{34}(Mo_5O_{19})_2(MoO_4)_2(OTf)_2(OH)_4]\cdot(OTf)_2$ (**4**). **3** and **4** have been structurally characterized and revealed to contain core−shell cluster architectures in which different numbers and kinds of POM templates are encapsulated.

The one-pot reaction of $Cu(BF_4)_2$, copper metallic powder, and $tBuC\equiv CH$ with $(NH_4)_6Mo_7O_{24}$ in MeOH at room temperature resulted in a gradual color change from bluish to red; after 12 h the solution was filtered and stored at −20 °C, which deposited red block-like crystals of $[Cu_{33}(tBuC\equiv C)_{24}(Mo_4O_{16})]\cdot BF_4$ (**3**) in 40% yield (see synthetic details in Supporting Information). Single-crystal X-ray analysis revealed that one full formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of **3**. The cationic component exhibits a "cluster-in-cluster" architecture in which a $Mo_4O_{16}^{8-}$ polyoxoanion is encapsulated within the Cu_{33} shell and stabilized with Cu(I)−O bonds in the range 2.012(8)−2.583(1) Å, which are comparable to the distances in reported Cu(I)-polyoxomolybdate compounds.[14] Overall charge balance against the cationic cluster is provided by one BF_4^- counteranion. The in-situ-generated $Mo_4O_{16}^{8-}$ template consisting of four edge-sharing MoO_6 octahedra (Figure 1a) differs from the frequently reported $Mo_4O_{16}^{8-}$ moiety with a planar Mo_4 group as well as those exhibiting a cubane-like Mo_4O_4 arrangement, and it is thus an unprecedented lacunary species.[15] Bond valence sum (BVS) calculation indicates that the Mo centers are all in the +6 oxidation state (BVS = 5.87−6.07, Table S1).[16]

The periphery of the bowl-shaped Cu_{33} shell is ligated exclusively by a total of 24 $tBuC\equiv C^-$ ligands through a combination of σ- and π-type bonding (Figure 1d). These ligands are distributed fairly uniformly, which makes the cationic cluster a nanoscale particle with approximate dimensions of 14 × 14 × 17 Å. Among these ligands, 20 take variable μ_3-η^1,η^1,η^1, μ_3-η^1,η^1,η^2 and μ_3-η^1,η^2,η^2 modes, two adopt the μ_2-η^1,η^2 mode, and the remaining two have μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^1$ and μ_6-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^1,\eta^1$ modes. The prevalence of μ_3 modes leads us to consider the Cu_{33} shell as composed of Cu(I) triangles that are fused to form lower and upper subshells (Figure 1b and 1c). The lower subshell takes a boat configuration assembled by two geometrically similar crown-like motifs sharing two Cu(I) vertices. Either crown-like motif is constructed of five corner-sharing Cu(I) triangles, which is further capped by an additional Cu(I) ion at the pole. The five
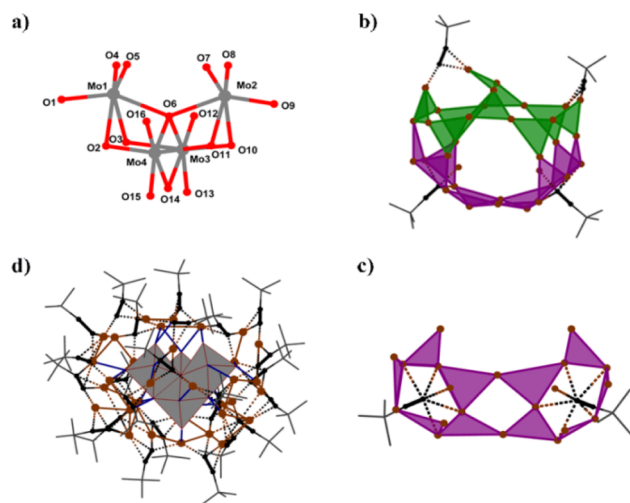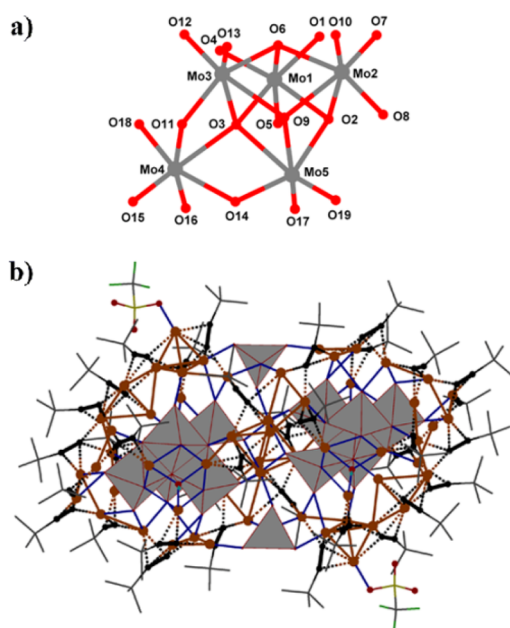

Figure 1. Illustration of the molecular cluster in $[Cu_{33}(tBuC\equiv C)_{24}(Mo_4O_{16})]\cdot BF_4$ (**3**). (a) Configuration of the $Mo_4O_{16}^{8-}$ polyoxoanion. (b) Cu_{33} shell constructed from Cu(I) triangles that are fused to form lower (purple) and upper (green) subshells. The upper subshell is enclosed by the μ_2 alkynide ligands and the lower subshell features the μ_5-η^1 and μ_6-η^1 alkynide ligands. The μ_3 ligands (each links three Cu(I) ions to form a triangle) are omitted for clarity. (c) Up−down view of the lower subshell highlighting the unprecedented μ_5-η^1 (left) and μ_6-η^1 (right) alkynide ligands. (d) Molecular structure of the cationic cluster. The encapsulated $Mo_4O_{16}^{8-}$ template is shown as gray edge-sharing octahedra. The ethynide groups are shown as thick black rods. The carbon atoms of the ethynide group are represented as small black balls, and their bonds to Cu(I) atoms are indicated by broken lines. Color code: Cu(I) = brown; Cu(I)−O connections = blue lines; Cu(I)··· Cu(I) contacts (<2.8 Å) = brown lines.

linked Cu(I) vertices are almost coplanar, forming a pentagon. Intriguingly, the μ_6 (or μ_5) ligand is oriented nearly perpendicular to the pentagon, which σ-bonds end-on to the capping Cu(I) ion and π-bonds side-on to five (or four) Cu(I) vertices of the pentagon. Such μ_5-η^1 coordination pattern is unprecedented, and binding six Cu(I) ions in a μ_6 mode is observed for the first time for the $tBuC\equiv C^-$ ligand. In the upper subshell, the Cu(I) triangles are arranged around the POM template in a cyclic fashion that also resembles a crown. The μ_2 ethynide ligands provide further enclosure leaving no significant crevice.

The Cu(I)−C bond distances of 1.84(2)−2.11(2) and 1.99(1)−2.58(1) Å correspond to σ and π interactions, which are in accord with the values observed in $[tBuC\equiv CCu]_{24}$.[5a] Cu(I)···Cu(I) contacts in the range 2.531(2)−2.765(6) Å are shorter than twice the van der Waals radius (2 × 1.40 Å) and indicate the presence of closed-shell cuprophilic interactions.[3,4]

A similar reaction using $Cu(OTf)_2$ instead of $Cu(BF_4)_2$ was conducted; after 12 h of stirring and removal of solvent, the residue was dissolved in CH_2Cl_2 and red needle-like crystals of **4** in a low but reproducible yield of 3% were deposited by diffusion of Et_2O into the CH_2Cl_2 solution (see synthetic details in Supporting Information). The crystal structure of **4** revealed a centrosymmetric, peanut-shaped aggregate (Figure 2b), formulated as $[Cu_{62}(tBuC\equiv C)_{34}(Mo_5O_{19})_2(MoO_4)_2(OTf)_2(OH)_4]\cdot(OTf)_2$. With 62 Cu(I) centers, it is the hitherto largest Cu(I) alkynyl cluster. The $Mo_5O_{19}^{8-}$ and MoO_4^{2-} units (Mo: BVS = 5.88−6.11, Table S1) were produced in situ by fragmentation of the

Figure 2. Illustration of the cluster structure in $[Cu_{62}(tBuC{\equiv}C)_{34}(Mo_5O_{19})_2(MoO_4)_2(OTf)_2(OH)_4]\cdot(OTf)_2$ (**4**): (a) $Mo_5O_{19}{}^{8-}$ polyoxoanion. (b) Molecular structure of the cationic cluster. The two encapsulated $Mo_5O_{18}{}^{8-}$ templates are shown as gray edge-sharing octahedra, and the two $MoO_4{}^{2-}$ ligands as gray tetrahedra. Color code: Cu(I) = brown; O = red; S = yellow; F = green; H = turquiose; Cu(I)−O connections = blue lines; Cu(I)···Cu(I) contacts (<2.8 Å) = brown lines.

$(NH_4)_6Mo_7O_{24}$ precursor, and the unprecedented geometry of the former species is built from a Mo_4O_4 cubane face-sharing with a MoO_6 octahedron (Figure 2a). Two $Mo_5O_{19}{}^{8-}$ lacunary polyoxoanions template inside the Cu_{62} shell with Cu(I)−O bond distances of 1.873(6)−2.516(1) Å.

The large cluster shell of **4** is consolidated by 34 $tBuC{\equiv}C^-$, 2 $MoO_4{}^{2-}$, 4 OH^- and 2 OTf^- ligands. The overall dimensions of the dicationic cluster are approximately $16 \times 20 \times 26$ Å. Of the 34 alkynyl ligands, 22 adopt the μ_3-η^1,η^1,η^2 mode, 8 have the μ_4-η^1,η^1,η^2 mode, 2 take the μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ mode and the remaining 2 adopt the μ_2-η^1,η^2 mode. Four μ_3−OH^- ligands each caps three Cu(I) ions, stabilizing the cluster surface with Cu(I)−O distances being 1.921(8)−2.102(8) Å. Two $MoO_4{}^{2-}$ ligands use the μ_5-$\kappa O{:}\kappa O'{:}\kappa O'{:}\kappa O''{:}\kappa O'''$ mode to make connections around the shell with bond distances of 1.816(10)−2.227(8) Å. Additionally, two μ_1-OTf^- ligands each bonds to one Cu(I) ion at a distance of 1.965(9) Å. Overall charge neutrality is achieved by two OTf^- counteranions, which form intramolecular hydrogen bonds with two nearby OH^- ligands (O···O, 2.72 Å). The driving force for the generation of small OH^- and $MoO_4{}^{2-}$ ligands is likely to be the spatial requirement during assembly, which allows some reductions of steric interactions at the cluster periphery. The formation of **4**, which involves in situ reactions and intricate assembly of multiple components, was ineffective (yield of <5%).

The σ- and π-type Cu(I)−C bonding distances are 1.84(1)−2.20(1) and 1.95(1)−2.59(1) Å, respectively, being similar to the corresponding values observed in **3**. The Cu(I)···Cu(I) contacts of 2.480(3)−2.791(2) Å also suggest the occurrence of cuprophilic interactions.

Overall, based on our new synthetic protocol, the designed synthesis of high-nuclearity Cu(I) clusters via the templating strategy has been achieved: that is, upon introduction of POM,

facile expansion of cluster nuclearity was observed to yield Cu_{33} and Cu_{62} nanoclusters (Scheme S1). In this process, the POM precursor underwent transformation to generate the corresponding $Mo_4O_{16}{}^{8-}$ and $Mo_5O_{19}{}^{8-}$ fragments; the resultant lacunary polyoxoanions with abundant terminal oxygen atoms and high charge densities[17] are favorable for the aggregation of more Cu(I) ions, which then function as templates to induce Cu(I) shell formation via the Cu(I)−O coordination bonding.[18] It appears plausible that $Mo_4O_{16}{}^{8-}$ and $Mo_5O_{19}{}^{8-}$ as cluster cores can also effectively disperse the positive charges on the Cu(I) shells. As far as we are aware, neither of the two species has been observed before as "stand-alone" polyoxoanions, and their ability in templating the core−shell molecular assembly is highlighted herein. The versatile $tBuC{\equiv}C^-$ ligand is also crucial for the formation of such assemblies. The space-filling models of **3** and **4** (Figure S4) clearly demonstrate how the bulky ligands effectively shield the Cu(I) shells, which enhances cluster stability, solubility and the tendency to self-assemble into macroscopically ordered crystals, thus allowing us to elucidate their structures by single-crystal X-ray diffraction.

The photoluminescent properties of **1**−**4** were investigated in the solid state at 298 K, and the photophysical data are summarized in Table S2. Upon excitation at λ > 330 nm, red luminescence was observed for complexes **1** and **2** with maximum emission centered at ca. 700 nm as shown in Figure 3. The lifetimes on a microsecond scale together with large
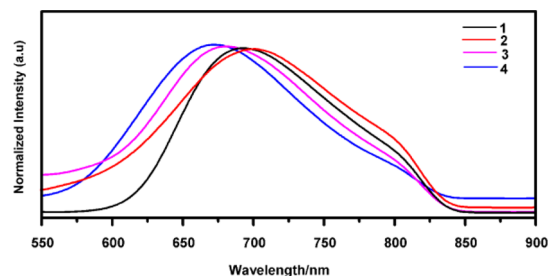
Figure 3. Normalized solid-state emission spectra of complexes **1**−**4** at 298 K.

Stokes shifts suggest that the emissions are associated with a spin-forbidden transition of triplet parentage. With reference to the spectroscopic studies of Yam, Ford and Chen, the emissions can be tentatively assigned as originating from the ^{3}LMCT $[tBuC{\equiv}C \rightarrow Cu_n]$ excited state, which is mixed with the Cu(I)-centered d-s/d-p characters that have been modified by cuprophilic interactions.[3e,f,19] Similar emission origin has been ascribed to the high-nuclearity Cu_{20} and $Ag_{16}Cu_9$ alkynyl complexes with comparable emission bands at 600−850 and 600−1100 nm, respectively.[5b,19a] These low-energy emissions relative to the previously reported polynuclear Cu(I) alkynyl clusters that usually emit at 450−650 nm[20] in the solid state result from the more pronounced cuprophilic interactions in these high-nuclearity clusters, as suggested by Chen.[19a] In contrast to **1** and **2**, it appears that coordination of POM templates to Cu(I) has an effect on the triplet excited state, as indicated by the blue-shifted emissions at 680 and 670 nm for **3** and **4**, respectively, which emit orange light under the same excitation wavelength.

In summary, we have developed a novel comproportionation-based synthetic route to discrete Cu(I) tert-butylethynide clusters. Synchronously, the scope has been expanded via

polyoxomolybdate templation to produce two high-nuclearity core—shell clusters. Our work provides insight into the structural aspects of Cu(I) alkynyl chemistry while creating a new synthetic paradigm. We expect that (i) the template-based approach holds good promise in the designed assembly of a diverse library of Cu(I) nanoclusters with intriguing structures and photophysical properties, and (ii) the comproportionation methodology can be applied to the facile synthesis of a widened range of Cu(I) coordination complexes stabilized by related carbon-rich alkynyl $RC\equiv C^-$ ligands. In fact, preliminary results have been obtained along both tracks, and further investigation is in progress.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12103.

Experimental details including syntheses of compounds **1−4**, IR, MS spectra, and additional figures and tables (PDF)

X-ray crystallographic data for **1−4** (CIF)

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Notes
The authors declare no competing financial interest.

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(11) This comproportionation reaction is applicable to various other CuX_2 salts (X = ClO_4^-, NO_3^-, SO_4^{2-}, $RCOO^-$ (R = CH_3, CF_3, CCl_3)), and the identity of resulting Cu(I) clusters depends on the coexisting anion employed. The results will be reported elsewhere.

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