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Template Synthesis

A Facile Template Approach to High-Nuclearity Silver(I) Alkynyl Clusters**

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Cluster compounds have attracted a great deal of attention because of their appealing structural beauty and fascinating properties.[1–4] The preparation of high-nuclearity clusters usually involves the complex assembly of multiple components; it is therefore a challenge to control the formation process of a cluster that contains many metal centers. One synthetic approach uses templates to induce the formation of cluster compounds.[5,6] Although cationic and neutral species have been extensively used as templates in synthetic chemistry, anion-templated synthesis has been received much less attention. Recent examples have shown that anion templates play an important role in the syntheses of cluster compounds.[7]

Metal alkynyl complexes can be used as versatile precursors for the synthesis of high-nuclearity silver clusters.[8,9] An elegant example is the novel halide-templated rhombohedral silver–alkynyl cage compounds $[Ag_{14}(C{\equiv}CtBu)_{12}X]^+$ (X = F, Cl, Br) reported by Vilar, Mingos and co-workers.[10] It is believed that halide ions are important for the formation of these types of silver clusters. We have recently shown that novel silver clusters could be isolated with the simultaneous templation of carbonates that were derived from the fixation of atmospheric carbon dioxide.[11] This serendipitous finding inspired us to carry out a rational investigation on the templating effects of other anions. Herein, we describe a facile approach to the synthesis of silver alkynyl clusters with a general structural type, which is exemplified by the application of tetrahedral anions as the directing agents (Figure 1). A series of novel high-nuclearity silver clusters have been isolated through such a synthetic approach:

$[Ag_{22}(C{\equiv}CtBu)_{18}(CrO_4)](BF_4)_2$ **1**

$[Ag_{21}(C{\equiv}CtBu)_{18}(SO_4)]BF_4$ **2**

$[Ag_{35}(C{\equiv}CPh)_{28}(CrO_4)_2(TMEDA)_4](BF_4)_3$ **3**

The cluster size and shape can be controlled by the introduction of different templating anions and the use of different alkynyl ligands (with various R groups). It is also demonstrated that a giant silver cluster with 35 silver(I) centers can be obtained through the double templation of two chromate ions.

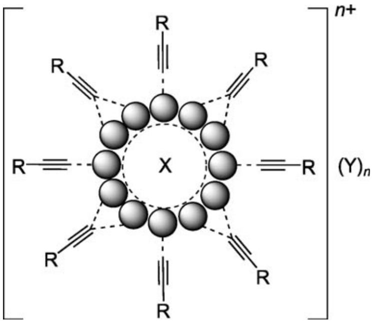

Figure 1. General structure of the cluster; X represents a templating anion, Y a counterion.

Complex **1** was obtained by the reaction of $[tBuC{\equiv}CAg]_n$ with $AgBF_4$, followed by the addition of $K_2Cr_2O_7$ in the presence of TMEDA (*N,N,N′,N′*-tetramethylethylenediamine). Under the reaction conditions (pH ≈ 8), $Cr_2O_7^{2-}$ ions became CrO_4^{2-} ions. The yellow color of the solution, which is characteristic of CrO_4^{2-} ions, indicated that these ions were successfully incorporated into the silver system. If all the CrO_4^{2-} ions had reacted with Ag^I ions, Ag_2CrO_4 would have formed as a red precipitate and the solution would be colorless. Yellow crystals of **1** were isolated by evaporation of the solution. The IR vibrations at 898 and 835 cm^{-1} confirmed the presence of the CrO_4^{2-} ion, and the bands at 2031 cm^{-1} and 1083 cm^{-1} were assigned to the C≡C groups and BF_4^- anions, respectively. Single crystal X-ray structural analysis[12] showed that **1** is a cationic cluster that consists of 22 silver atoms consolidated by 18 alkynyl ligands and one interstitial chromate ion (Figure 2).

The ball-shaped skeleton of **1** is composed of silver(I) triangles, tetragons, and pentagons. The templating CrO_4^{2-} ion sits inside the silver cage and the shortest Ag–O bond distance is 2.634 Å, which indicates that the CrO_4^{2-} ion binds loosely to the silver(I) shell. The CrO_4^{2-} ion is slightly distorted from tetrahedral coordination with bond angles in the range 105.1(8)–112.3(6)°. Each $tBuC{\equiv}C$ ligand adopts μ_3-η^1, η^1, η^1 or μ_3-η^1, η^1, η^2 bridging modes to link a silver(I) triangle, and a total of 18 ligands are peripherally coordinated to silver atoms in order to hold the cluster together. Tetrafluoroborate counterions are located in the space between cationic clusters to balance the charge of the complex.

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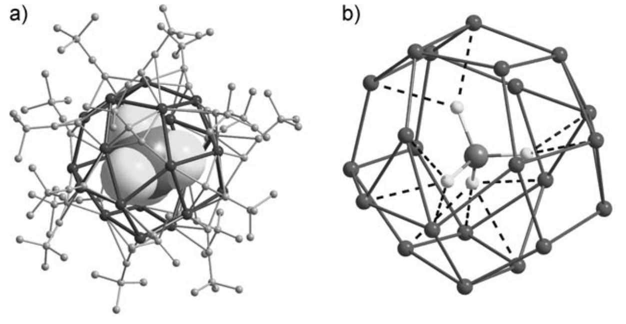

Figure 2. a) Structure of the cationic part of $[Ag_{22}(C{\equiv}C\mathit{t}Bu)_{18}(CrO_4)](BF_4)_2$ **1**. The templating chromate ion is shown in space-filling mode. Hydrogen atoms and Ag–O bonds are omitted for clarity. b) Ball-shaped core structure in **1**.

By using the SO_4^{2-} ion instead of the CrO_4^{2-} ion in the same preparative procedure, a new silver cluster **2** was isolated. The IR vibration at 1124 cm^{-1} confirmed the presence of the SO_4^{2-} ion in **2**, and the bands at 2028 and 1080 cm^{-1} were assigned the C≡C groups and BF_4^- anions, respectively. Structural determination indicated that **2** is also a cage compound with a lower nuclearity. As shown in Figure 3, an SO_4^{2-} ion is enclosed in the silver cage that comprises 21 silver atoms. There are also 18 peripheral alkynyl ligands that hold the cluster together. The Ag–O bond distances are shorter than those in **1**; the shortest Ag–O connection is 2.483(8) Å for O1, and 2.554(7) Å for O2. Only weak interactions occur between O3 (or O4) and the silver atoms, with the shortest Ag–O distance of 2.651 Å for O3 and 2.667 Å for O4. The SO_4^{2-} ion exists as an almost regular tetrahedron with bond angles in the range 108.1(4)–111.8(4)°. Because the interstitial SO_4^{2-} ion is a smaller tetrahedral ion than CrO_4^{2-} (the S–O bond length is approximately 0.1 Å shorter than the Cr–O bond length), the expected templating effect was observed, that is, a smaller cluster was obtained with the SO_4^{2-} ion. The configuration of the cationic cluster changed from ball-shaped in **1** to oval in **2**, that of **2** is formed by simply removing one $AgBF_4$ from **1** ($CrO_4^{2-}@Ag_{22}$ in **1** versus $SO_4^{2-}@Ag_{21}$ in **2**).

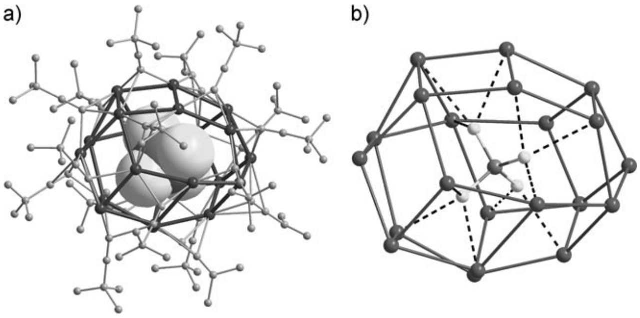

Figure 3. a) Molecular structure of the cationic part of $[Ag_{21}(C{\equiv}C\mathit{t}Bu)_{18}(SO_4)]BF_4$ **2**. The templating sulfate ion is showed in space-filling mode. Hydrogen atoms and Ag–O bonds are omitted for clarity. b) The oval core structure in **2**.

Attempts have also been made to study the influence of space hindrance by using the flat PhC≡C instead of the bulky *t*BuC≡C ligand. To our surprise, a peanut-shaped cage that was doubly templated by two CrO_4^{2-} ions was found in the structure of **3**. The IR vibrations at 906 and 836 cm^{-1} confirmed the presence of the CrO_4^{2-} ion, and the bands at 2025 cm^{-1} and 1065 cm^{-1} were assigned to the C≡C groups and BF_4^- ions, respectively. Interestingly, structural determination revealed that the cation of **3** is a giant cluster that consists of 35 silver centers $[(CrO_4^{2-})_2@Ag_{35}]$ (Figure 4). A total of 28 peripheral ligating alkynyl ligands surround the cluster. The structure has pseudo-twofold symmetry, with four silver atoms, each of which are chelated by a TMEDA ligand in the corner of the cluster. The core configuration can be taken as two single cages of $CrO_4^{2-}@Ag_{20}$ that are joined by five shared silver atoms (Figure 5). Complex **3** represents the first example of a cluster that involves the double templation of two chromate ions, and features the largest silver alkynyl cluster reported to date.

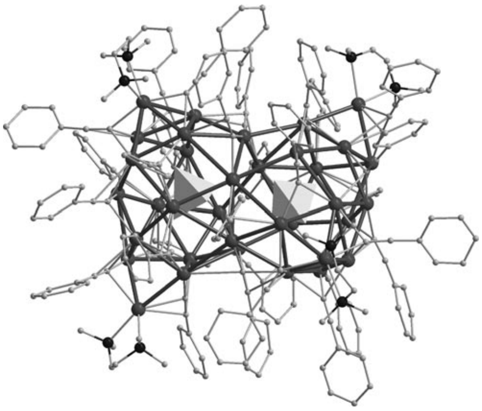

Figure 4. The molecular structure of the cationic part of $[Ag_{35}(C{\equiv}CPh)_{28}(CrO_4)_2(TMEDA)_4](BF_4)_3$ **3**. The templating chromate ions are illustrated as tetrahedra. Hydrogen atoms and Ag–O bonds are omitted for clarity.

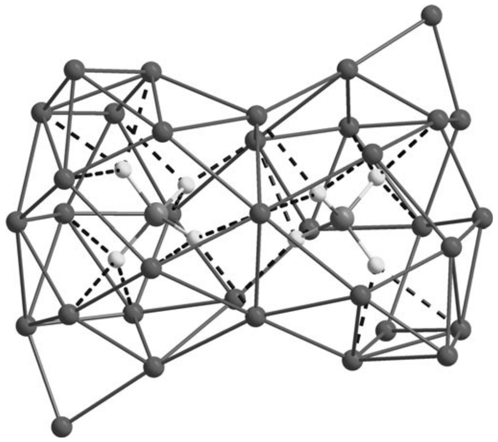

Figure 5. The peanut-shaped core structure in **3**.

When **2** was dissolved in MeOH, a color change was observed, which implies that **2** decomposes in solution. However, NMR spectra indicate that the solid structures of **1** and **3** were retained in methanolic solution (see the Supporting Information). Clean ^{1}H and ^{13}C NMR spectra of **1** in CD_3OD were recorded, and the observed peaks were in agreement to the corresponding structure. In addition, the ^{1}H NMR spectrum of **3** in CD_3OD shows three peaks that integrate in a ratio of 140:16:48, which is consistent with the number of hydrogen atoms in phenyl groups, as well as the CH_2 and CH_3 groups in TMEDA. The ^{13}C NMR data are also consistent with the determined structure.

Although TMEDA was not incorporated in clusters **1** and **2**, we were not able to isolate any cluster compounds in the absence of TMEDA. The role of TMEDA is not clear in the syntheses of the silver clusters, but it is conceivable that TMEDA is helpful for the formation of certain intermediates by chelating the silver ions.

In summary, we have presented a facile approach for the synthesis of high-nuclearity silver clusters by templating the assembly of silver alkynyl precursors with anions. It is predicted that the results described in this work is only a fraction of the area that remains to be explored. Further investigation of various factors that influence the formation of the silver alkynyl clusters is in progress.

Experimental Section

Synthesis of **1**: AgC_2tBu (0.0830 g, 0.439 mmol) was dissolved in a solution of $AgBF_4$ (0.0430 g, 0.221 mmol) in methanol (4 mL) under ultrasonication. TMEDA (0.0509 g, 0.438 mmol) was added and a clear solution was obtained, to which $K_2Cr_2O_7$ (0.0100 g, 0.034 mmol) was added under stirring. After 3 h, a yellow suspension was obtained, and a yellow solution was collected by filtration. Slow evaporation of this solution afforded the product as yellow crystals. Yield: 63.2 % (0.0600 g). Elemental analysis (%) calcd for $Ag_{22}B_2F_8CrO_4C_{108}H_{162}$: C 31.46, H 3.96; found: C 31.42, H 3.96; IR (KBr): $\tilde{\nu} = 2031$ (vs, C≡C), 1083 (vs, BF_4^-), 898, 835 cm^{-1} (vs, CrO_4^{2-}).

Synthesis of **2**: 0.1770 g (0.936 mmol) AgC_2tBu was dissolved in a solution of $AgBF_4$ (0.0910 g, 0.467 mmol) in methanol (8 mL) under ultrasonication. TMEDA (0.1090 g, 0.933 mmol) was added and a clear solution was obtained, to which Na_2SO_4 (0.0100 g, 0.070 mmol) was added under stirring. After 3 h, a white suspension was obtained, and a colorless solution was collected by filtration. Slow evaporation of the clear solution afforded the product as colorless crystals. Yield: 41.7 % (0.0843 g). Elemental analysis (%) calcd for $Ag_{21}BF_4SO_4C_{108}H_{162}$: C 33.19, H 4.18; found: C 33.50, H 4.65; IR (KBr): $\tilde{\nu} = 2028$ (vs, C≡C), 1124 (vs, SO_4^{2-}), 1080 cm^{-1} (vs, BF_4^-).

Synthesis of **3**: AgC_2Ph (0.0696 g, 0.333 mmol) was dissolved in a solution of $AgBF_4$ (0.0324 g, 0.166 mmol) in methanol (4 mL) under ultrasonication. TMEDA (0.0387 g, 0.333 mmol) was added and a white suspension was obtained. After the solvent was removed under reduced pressure, a yellow solid was formed and was dissolved in methanol/chloroform (1:1, 6 mL). $K_2Cr_2O_7$ (0.0032 g, 0.011 mmol) was added under stirring to the resulting solution. After 3 h, a yellow suspension was obtained, and a yellow solution was collected by filtration. Slow evaporation of this solution afforded the product as yellow crystals. Yield: 59.5 % (0.0402 g). Elemental analysis (%) calcd for $Ag_{35}B_3F_{12}Cr_2O_8C_{248}H_{204}N_8$: C 39.37, H 2.71, N 1.48; found: C 39.34, H 2.72, N 1.41; IR (KBr): $\tilde{\nu} = 2025$ (vs, C≡C), 906, 836 (vs, CrO_4^{2-}), 1065 cm^{-1} (vs, BF_4^-).

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[12] Crystal data for **1**: $[C_{108}H_{162}B_2O_4F_8CrAg_{22}]$, monoclinic, $P2_1/n$, $a = 21.8762(5)$, $b = 21.6612(6)$, $c = 28.2026(8)$ Å, $\beta = 91.033(2)$, $V = 13362.0(6)$ Å^3, $Z = 4$, $T = 173$ K, 77080 reflections measured, 35799 unique ($R_{int} = 0.148$), final $R1 = 0.0529$, $wR2 = 0.0723$ for 8235 observed reflections $[I > 2\sigma(I)]$. Crystal data for **2**, $[C_{108}H_{162}B\,O_4F_4SAg_{21}]$, monoclinic, Pn, $a = 15.3810(3)$, $b = 15.7752(4)$, $c = 27.3409(5)$ Å, $\beta = 94.834(2)$, $V = 6610.4(2)$ Å^3, $Z = 2$, $T = 173$ K, 47221 reflections measured, 27050 unique ($R_{int} = 0.0548$), final $R1 = 0.0438$, $wR2 = 0.0708$ for 11807 observed reflections $[I > 2\sigma(I)]$. Crystal data for **3**, $[C_{248}H_{204}B_3N_8O_8F_{12}Cr_2Ag_{35}]$, monoclinic, $P2_1/c$, $a = 37.3001(9)$, $b = 19.6190(3)$, $c = 36.5984(7)$ Å, $\beta = 112.173(3)$, $V = 24801.8(9)$ Å^3, $Z = 4$, $T = 173$ K, 101441 reflections measured, 38002 unique ($R_{int} = 0.1424$), final $R1 = 0.0760$, $wR2 = 0.1607$ for 14639 observed reflections $[I > 2\sigma(I)]$. CCDC 729707 (**1**), CCDC 729708 (**2**) and CCDC 729709 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.