Cluster Compounds

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A Giant Silver Alkynyl Cage with Sixty Silver(I) Ions Clustered around Polyoxometalate Templates**

*Juan Qiao, Kang Shi, and Quan-Ming Wang**

Chemical templates play an important role in the formation of complex systems containing multiple components which have well-defined finite structures of large size, sometimes on the nanoscale.[1] Compared with the widely studied templation by cations and neutral compounds, anion templation has been much less developed in synthetic chemistry. However, it has been increasingly recognized that anionic templates are very useful in preparing metalla-assemblies. Many inorganic polyatomic anions have been utilized in the construction of finite assemblies, and the size and shape of the directing anions dictate the geometry and connectivity of the final structures.[2–4]

Recently, we developed a facile template approach for the synthesis of high-nuclearity silver(I) alkynyl clusters,[5] and a variety of silver clusters have been isolated with spherical chloride, triangular carbonate, and tetrahedral chromate templates.[5,6] Considering that polyoxometalates (POMs) are large oxo anions of group 6 or 5 elements and have good affinity to silver ions,[7–10] we attempted to incorporate POMs into silver alkynyl systems. The advantages of employing a clusterlike POM anion as template lie not only in increasing the nuclearity of silver clusters but also in introducing new redox centers that can profoundly affect the physical properties of the cluster.

We expected that it would be difficult to obtain structural information on the products, because of the insolubility of silver polyoxometalates. Fortunately, we found that the solvothermal method worked well in our silver alkynyl/POM system, and giant silver cluster $[Ag_{60}(Mo_6O_{22})_2(t\mathrm{BuC{\equiv}C})_{38}](CF_3SO_3)_6$ (**1**), which is the largest silver alkynyl cluster so far, was isolated by using the POM templating strategy under solvothermal conditions. Surprisingly, incorporation of polyoxomolybdate stabilizes the silver cluster and makes it insensitive to light. Furthermore, cyclovoltammetric studies revealed that electronic communication exists between POM core and Ag_{60} shell. Herein we report the synthesis, structure, and redox behavior of this novel POM-templated silver cluster.

The reaction of $t\mathrm{BuC{\equiv}CAg}$ with $AgCF_3SO_3$ in methanol in the presence of $(NH_4)_6Mo_7O_{24}$ led to the formation of a white solid, which was then solvothermally treated to give **1** as colorless crystals in moderate yield. A similar procedure with $AgBF_4$ in place of $AgCF_3SO_3$ gave a compound isostructural to **1**.

The composition of **1** is supported by elemental analysis. An IR band at 2013 cm^{-1} confirmed the presence of the C≡C group in **1**; the band at 823 cm^{-1} is assigned to the Mo–O vibration; and the bands at 1159 and 1046 cm^{-1} are due to the triflate anion. The structure of **1** was established by single-crystal X-ray structure analysis,[11] which revealed that the cationic part of **1** is a giant cluster consisting of 60 silver atoms peripherally bridged by 38 alkynyl ligands with double templation by two in-situ-generated $Mo_6O_{22}^{8-}$ anions. The bulk of the sample was confirmed to be uniform by comparing the measured X-ray powder diffraction pattern with that simulated from single-crystal data (see the Supporting Information).

The precursor $Mo_7O_{24}^{6-}$ was transformed into $Mo_6O_{22}^{8-}$ under the reaction conditions. The unprecedented configuration of this hexanuclear moiety is built from six edge-sharing MoO_6 octahedra and shows a Mo_4O_4 cubane with two additional Mo atoms attached (Figure 1 a,b). This structure is different from those of other known $Mo_6O_{22}^{8-}$ moieties, which have incomplete-cubane or double-cubane arrangements.[12]

The centrosymmetric structure of **1** (Figure 1 c) has a peanutlike skeleton with an Ag_{60} shell and two $Mo_6O_{22}^{8-}$ nuts (Figure 1 d). The cluster is nanosized with approximate dimensions of 3.0 × 2.0 nm. Two $Mo_6O_{22}^{8-}$ ions act as templates for the formation of the silver cluster, with the Ag–O bond lengths varying from 2.039(6) to 2.573(5) Å, which are comparable to the values of 2.296(3)–2.581(2) Å found in $[Ag_4(\mathrm{dmso})_8(Mo_8O_{26})]_n$.[13] A total of 38 $t\mathrm{BuC{\equiv}C}$ ligands adopt μ_3 or μ_4 (with only two exceptional μ_2) bridging modes to coordinate silver atoms peripherally and hold the cluster together. Four triflate anions are loosely bound to silver atoms with O–Ag distances longer than 2.6 Å (O101–Ag15 2.615; O101–Ag9 2.736; O203–Ag30 2.805), and the other two are present as counterions in the space between cationic clusters to balance the charge. These coordination sites for triflate anions are important in electrochemical measurements, because the cationic cluster could be immobilized in Nafion matrix.

Because cluster **1** is soluble in methanol, its solution behavior was investigated by ESI-MS and NMR (see the Supporting Information). The ESI mass spectrum did not give meaningful results, as the highly charged cluster cation was

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[*] J. Qiao, Dr. K. Shi, Prof. Dr. Q.-M. Wang
State Key Lab of Physical Chemistry of Solid Surfaces
Department of Chemistry, College of Chemistry and Chemical Engineering
Xiamen, 361005 (P. R. China)
Fax: (+86) 592-218-3047
E-mail: qmwang@xmu.edu.cn

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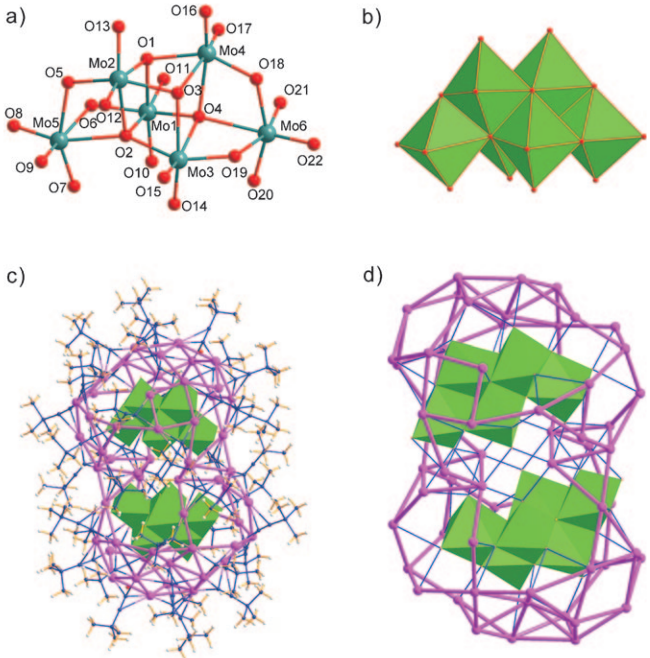

Figure 1. a) Ball-and-stick view, b) polyhedral representation of the $Mo_6O_{22}^{8-}$ ion. c) Molecular structure of the cationic part of **1**. $Mo_6O_{22}^{8-}$ ions are shown as green edge-sharing octahedra, and Ag atoms as purple balls. d) Core structure illustrating the silver–POM interactions. Ag⋯Ag contacts shorter than 3.4 Å are drawn as purple bonds, and blue lines indicate the Ag–O connections.

labile during the ESI process.[14] The proton NMR spectrum of **1** in $CDCl_3$ displayed broad signals around 1.43 ppm from the methyl groups of the *t*BuC≡C⁻ ligands, which is attributed to the general contribution of the alkynyl ligands coordinated at different silver centers. Based on the NMR data and the fact that **1** can be recovered from solution by recrystallization, it appears that the cationic cluster may be intact in solution.

Since $Mo_6O_{22}^{8-}$ and silver(I) species are both redox centers, it was interesting to see whether electronic communication occurs between the $Mo_6O_{22}^{8-}$ and silver(I) ions. Cyclovoltammetric measurements were performed to study the electrochemical behavior of **1**.

The voltammetric response of a GC/**1**-NF electrode in $HClO_4/NaClO_4$ aqueous solution is shown as black lines in Figure 2 (GC and NF denote glassy carbon and Nafion, respectively). The detailed electrochemical reaction of **1** shows two couples of redox peaks with mean peak potentials of $E_{pc} = 0.025$, $E_{pa} = 0.044$ V (I) and $E_{pc} = -0.093$, $E_{pa} = -0.080$ V (II) within the potential range investigated. The peak-to-peak separations between the corresponding anodic and cathodic peaks (ΔE_p) are 0.019 (I) and 0.013 V (II), that is, two reversible redox processes.[15] The voltammetric response of a GC/MO-NF (MO = $Mo_7O_{24}^{6-}$) electrode (red lines in Figure 2) also displays two couples of redox peaks with mean peak potentials of $E_{pc} = 0.000$, $E_{pa} = 0.024$ V (I′), $E_{pc} = -0.118$, $E_{pa} = -0.100$ V (II′). All anodic and cathodic peak potentials of the $Mo_7O_{24}^{6-}$ anion are negatively shifted by about 0.02 V compared with that of **1**. The similar electrochemical behavior of GC/**1**-NF and GC/MO-NF indicates that the redox reaction of **1** originates from $Mo_6O_{22}^{8-}$, which is similar to analogous compounds reported in the literature.[16] To our surprise, no redox peaks from Ag^0/Ag^+ couples were observed. The only explanation is that the Ag_{60} shell functions as an electronic relay to transfer electrons to the $Mo_6O_{22}^{8-}$ clusters. The sulfonate groups of the Nafion matrix replace the triflate anions of **1** and stabilize the cationic cluster deposited on the modified electrode during the electrochemical redox process. To verify this hypothesis, the voltammetric response of a GC/**1** electrode was investigated; it only displayed a couple of redox peaks (blue lines in Figure 2). Comparative experimental results demonstrated that such a redox reaction corresponds to the deposition and dissolution of metallic silver species, that is, **1** decomposed in the redox process in the absence of Nafion matrix. Additional evidence is that the voltammetric response of GC/$AgCF_3SO_3$-NF is the same as that of GC/**1**, which indicates that peaks from Ag^0/Ag^+ couples should have been observed if decomposition took place on the GC/**1**-NF electrode. The core–shell electronic communication in **1** makes the silver cluster stable, that is, in the solid state, cluster **1** is not sensitive to light, and can be kept under ambient light without decomposition for months.

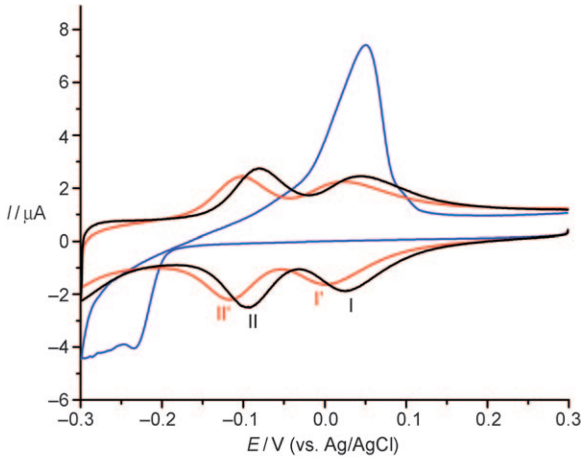

Figure 2. Cyclovoltammetric diagram of modified electrodes in degassed 0.1 M $HClO_4$ + 0.1 M $NaClO_4$ aqueous solutions at a scan rate of 0.1 V s⁻¹: black: GC/**1**-NF; red: GC/MO-NF; blue: GC/**1**.

In summary, a novel giant POM-templated silver cluster has been isolated and represents a new class of redox-active silver clusters: cluster-templated clusters. The electronic communication between POM cores and silver cluster shell implies various potential applications. Further work on the templating effects of iso- and heteropolyoxometalates is in progress.

Experimental Section

Caution! Due to the explosive nature of silver alkynyls, great care should be taken and only small amounts should be used.

Synthesis of **1**: *t*BuC≡CAg (0.0391 g, 2.07 mmol) was dissolved in a solution of AgOTf (0.0531 g, 4.82 mmol) in methanol (6 mL) under ultrasonication. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.0248 g, 0.2 mmol) and H_2O (0.3 mL) were added to the resulting solution, which was stirred for 3 h to give a white suspension. The reaction mixture was sealed and kept at 70 °C for 20 h. After cooling to room temperature, the solution was filtered and the filtrate evaporated slowly at room temperature in an Erlenmeyer flask. Complex **1** deposited as colorless crystals, which were washed with methanol and Et_2O. Yield: 37.3% (0.0251 g). C,H analysis (%) calcd for $Ag_{60}C_{234}Mo_{12}F_{18}H_{342}O_{62}S_6$: C 22.84, H 2.80; found: C 22.71, H 2.81; IR (KBr): $\tilde{\nu} = 2013$ (vs, C≡C); 1159, 1046 (vs, OTf); 823 cm^{-1} (Mo–O).

Voltammetric experiments were carried out in a degassed 0.1 M $HClO_4$ aqueous solution containing 0.5 M $NaClO_4$ at room temperature ((25 ± 2) °C) with a conventional three-electrode cell consisting of a GC working electrode (3 mm diameter), a platinum foil auxiliary electrode, and a home-made silver/silver chloride (Ag/AgCl) wire as reference electrode.

The GC electrode was polished with 0.3 μm alumina slurry and was subsequently ultrasonicated in ethanol and double-distilled water. 2 μL of an ethanolic solution containing **1** (35 μM) and 0.5% Nafion was dropped onto the pretreated GC electrode surface by using a microliter pipette and allowed to dry at room temperature to form the GC/**1**-NF electrode. For comparison, GC/MO-NF and NF/GC electrodes were also prepared by the same procedure.

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[11] Crystal data for **1**: $C_{234}H_{342}O_{62}S_6F_{18}Mo_{12}Ag_{60}$, $a = 43.7791(7)$, $b = 20.6639(3)$, $c = 41.8802(4)$ Å, $\beta = 101.907(1)°$, $V = 37071.6(9)$ Å^3, space group $C2/c$, $Z = 4$, $T = 223$ K, 160630 reflections measured, 50055 unique ($R_{int} = 0.0659$), final $R1 = 0.0557$, $wR2 = 0.1232$ for 20123 observed reflections [$I > 2\sigma(I)$]. CCDC 756502 (**1**) contains 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.

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