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Acid-Induced Surface Functionalization of Polyoxometalate by Enclosure in a Polyhedral Silver−Alkynyl Cage

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Received September 17, 2009; E-mail: tcwmak@cuhk.edu.hk

Polyoxometalates (POMs) exhibit a rich structural variety[1] and have potential applications in diverse areas.[2] In the pursuit of functional materials with novel architecture and desirable properties, considerable attention has been directed to the construction of POMs with transition metal or metal−organic subunits.[3]

Due to its high affinity to O donor ligands, the silver(I) ion has been used to functionalize POMs, and diverse Ag(I)−POM complexes have been obtained.[4,5] However, to date there is no reported example of any Ag(I) or transition metal modified[6−8] POM complex that has a POM anion encapsulated in a metal cluster cage. Hence the development of a general approach to the functionalization of POMs with metal clusters presents a challenging pursuit in current POM chemistry. The motivation in this respect lies in not only the controllable construction of large clusters from known POM building blocks but also the rational design of nanoscopic clusters possessing predetermined structures and functions via a bottom-up route.

Unlike other silver(I)−organic structure building blocks, the weak interactions between silver(I) and ethynide groups favor the onset of multiple argentophilic Ag···Ag interactions which overcome electrostatic repulsion between formal Ag(I) centers.[9] Thus large-nuclearity silver(I) aggregates are attainable by encapsulation of suitably chosen template building units.[10] The recent report of small tetrahedral oxoanion templated silver(I)−alkynyl clusters[11] prompted us to explore the encapsulation of polyoxometalate anions based on the $\mathrm{Ag}_n\subset\mathrm{C{\equiv}C^tBu}$ ($n = 4, 5$) supramolecular synthon,[12] which constitutes a part of our effort to create a new functionalized POM family incorporating silver(I)−ethynide[12] and −ethynediide[13] cluster units.

In this work, two novel monomeric silver(I)−alkynyl clusters encapsulating different polyoxometalates, $[\mathrm{Ag_{40}(C{\equiv}C^tBu)_{22}(CF_3{-}COO)_{12}(V_{10}O_{28})]\cdot 4CH_3OH}$ (**1**) and $[\mathrm{Ag_{40}(C{\equiv}C^tBu)_{20}(CF_3COO)_{12}(Mo_6O_{22})]\cdot 2CH_3OH}$ (**2**), have been obtained by an acid-induced facile approach. Their cluster structures and nanoscopic morphologies have been elucidated. Both of the polyoxoanions in **1** and **2** are encapsulated in respective cationic silver(I)−alkynyl cluster shells consolidated by multiple argentophilic Ag···Ag interactions. For the first time, the polyoxometalate ions are functionalized by silver(I) cages to form members of a new Ag(I)−POM family. Moreover, these two complexes are both neutral materials, in which the number of ^{t}BuC≡C$^-$ groups decreases along with the increasing negative charge of the central polyoxoanion. Such precise charge balance is unprecedented among known hybrid POMs, thereby offering the prospect of specific cluster-to-cluster transformation.

Most POMs can be isolated in aqueous solutions at different pH values, suggesting that acidity plays an important role in the formation of various polyoxometalate species.[14] However, by means of cryospray mass spectrometry, it has been shown that the isopolymolybdate anion in organic solution containing silver(I) cations undergoes isomerization to form other species.[5a] To achieve acidic conditions for the stabilization of polyoxometalates in an organic medium, we herein developed a new synthetic route by employing $\mathrm{CF_3COOH}$ as a trigger component. In this approach, the introduced acid acts not only as an agent to hydrolyze some of the AgC≡C^{t}Bu units but also as an effective acid source to hinder the disintegration of polyoxoanions into low-nuclearity species. By reacting the polyoxometalate organic salts ($\mathrm{(Et_4N)_3[H_3V_{10}O_{28}]}$ and $\mathrm{(^tBu_4N)_2[Mo_6O_{19}]}$) in turn with AgC≡C^{t}Bu and $\mathrm{CF_3COOH}$ in methanol, complexes **1** and **2** were successfully isolated as polyhedral silver(I)−alkynyl clusters encapsulating $[\mathrm{V_{10}O_{28}}]^{6-}$ and $[\mathrm{Mo_6O_{22}}]^{8-}$ polyoxoanions, respectively.[15] To confirm the validity of our synthetic strategy, two other cluster compounds, $[\mathrm{Ag_{24}(C{\equiv}C^tBu)_{14}(CF_3COO)_6(V_2O_7)]\cdot 2CH_3OH}$ (**3**) and $[\mathrm{Ag_{20}(C{\equiv}C^tBu)_{13}(CF_3COO)_5(MoO_4)]}$ (**4**), were synthesized under basic conditions using $\mathrm{AgCF_3COO}$ and AgC≡C^{t}Bu as the reactants (see Supporting Information). Though the same polyoxometalate salts were employed as starting materials, only small encapsulated oxoanions $[\mathrm{V_2O_7}]^{4-}$ and $[\mathrm{MoO_4}]^{2-}$ exist in **3** and **4**, respectively. Thus the presence of $\mathrm{CF_3COOH}$ in the reaction system enhances the stability of high-nuclearity polyoxometalate anions.

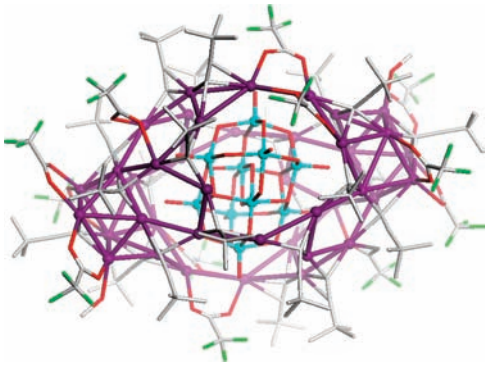

Figure 1. A perspective view of complex **1** (H atoms and bonds between Ag and O atoms of $[\mathrm{V_{10}O_{28}}]^{6-}$ are omitted for clarity; Color code: V, cyan; O, red; Ag, dark violet; C, gray; F, green).

Single-crystal X-ray analysis[16] revealed that complex **1** is a neutral ellipsoidal C_{2h} cluster consisting of forty silver(I) ions stabilized by centripetal ethynyl, peripheral trifluoroacetate (TFA) and methanol ligands along with a $[\mathrm{V_{10}O_{28}}]^{6-}$ polyoxoanion at its center (Figure 1). Sixteen ^{t}BuC≡C ligands adopt μ_3-η^1,η^1,η^1 or μ_3-η^1,η^1,η^2 ligation modes to link different silver triangles, while the other six use the μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$ or μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ mode to coordinate to planar or butterfly silver tetragons. Twelve TFA ligands link the neighboring silver(I) ions by μ_2-η^1,η^1 or μ_2-η^1,η^2 bridging modes, which also act as effective counterions to balance the charge. The central unprotonated $[\mathrm{V_{10}O_{28}}]^{6-}$ anion comprises ten edge-sharing $\mathrm{VO_6}$ octahedra with approximate D_{2h} symmetry. The surface oxygen atoms can be classified as terminal and μ_2-, μ_3-, μ_4-bridging

10.1021/ja907900b

types that possess different charge densities.[17] These oxygen atoms show different coordination behavior to the outer silver(I) ions, which are reflected by different V−O distances. Four terminal O atoms (O1, O14, O1a, O14a) coordinate to silver(I) ions with an average V−O distance of 1.629 Å, while the other four terminal O atoms (O3, O5, O3a, O5a) with an average V−O distance of 1.582 Å are not involved (Figure 2). The silver(I) ions around O1, O14, O1a, and O14a atoms do not form the usual triangles or tetragons but construct irregular silver pentagons. There also exist silver tetragons on top of the pentagons to form unusual asymmetrical silver prisms. These subunits reflect that the protruding terminal O atom with lower coordination ability is more favorably stabilized by the surrounding silver(I) pentagons. In contrast, the bridging O atoms in **1** show excellent coordination abilities, and most of them effectively link the silver(I) ions by Ag−O bonding interactions in the range of 2.452(7)−2.928(7) Å.

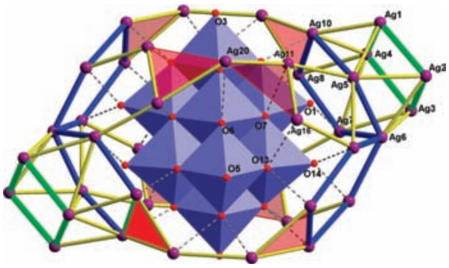

Figure 2. A combined view of complex **1** (all the ethynyl and TFA liands are omitted; silver triangles, tetragons, and pentagons are highlighted; atom color code: O, red; Ag, dark violet).

The most interesting structural feature is the fact that some triples of bridging O atoms compatibly connect with $Ag_3{\subset}C{\equiv}C^tBu$ units by Ag−O bonds to form distorted $\{Ag_3O_3\}$ trigonal prisms. Generally, each $R{-}C{\equiv}C^-$ ($R = {}^tBu$, Ph) ligand tends to attach to a silver triangle or tetragon, and the resulting assemblies are then fused together to form various silver-abundant clusters.[18] Thus the silver triangle is one of the important building units in the construction of silver-rich clusters. As such the ion-pair matching between the $Ag_3{\subset}C{\equiv}C^tBu$ synthon and triply bridging O atoms in **1** plays an important role in the crystal growth. Such special ion-pair recognition[19] is first observed among the known anion-based silver(I)−alkynyl compounds, which allows us to better understand the reaction between oxygen-abundant polyoxoanions and silver(I)−alkynyl shells and also devise a new route to the rational design of POM-based silver(I)−alkynyl complexes.

Complex **2** is also a neutral C_{2h} cluster with an ellipsoidal shape. As shown in Figure 3, an *in situ* generated $[Mo_6O_{22}]^{8-}$ anion occupies the center of the 40-vertex silver cluster. The outer silver(I) shell is occupied by 20 alkynyl, 12 TFA, and 2 methanol ligands that hold the silver cluster together. Though the $[Mo_6O_{22}]^{8-}$ anion has been reported very recently,[20] many elongated distances between Mo^{6+} centers and terminal O atoms are observed in complex **2**. The $Mo{-}O_t$ (O_t, terminal O atom) distances ranging from 1.738(7) to 1.772(6) Å in **2** are considerably longer than those observed (1.698−1.715 Å) in the reported $[Mo_6O_{22}]^{8-}$ anion. Thus the coordination abilities of the surface O atoms of the $[Mo_6O_{22}]^{8-}$ anion in **2** are significantly modified. This result can be confirmed by the fact that the interactions between the silver(I) shell and the central $[Mo_6O_{22}]^{8-}$ polyoxoanion are dramatically different from those in complex **1**, yielding markedly shorter $Ag{-}O_b$ (O_b, bridging O atom) distances of 2.205(6)−2.691(7) Å. Moreover, the terminal O atoms all coordinate to the shell vertices with $Ag{-}O_t$ (O_t, terminal O atom) distances in the range of 2.304(6)−2.699(8) Å. The ion-pair recognition between a triple of bridging O atoms and a $Ag_3{\subset}C{\equiv}C^tBu$ unit, however, is not predominant in **2**, as only two such connections are found (Figure 4). As compared to **1**, more silver tetragons and pentagons are present with stabilization by μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$ or μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ alkynyl and μ_2-η^1,η^1 TFA ligands, respectively. This geometric arrangement of silver(I) centers is similar to that in the SO_4^{2-} templated silver cluster,[11] showing that a central tetrahedral oxoanion is better stabilized by a polyhedral outer shell composed of silver tetragons and pentagons rather than silver triangles. In view of the higher symmetry of the central $[Mo_6O_{22}]^{8-}$ species, the silver cage is more regular and compact with a much smaller size (longest Ag···Ag separation of 14.309 Å) than that of **1** (17.665 Å).

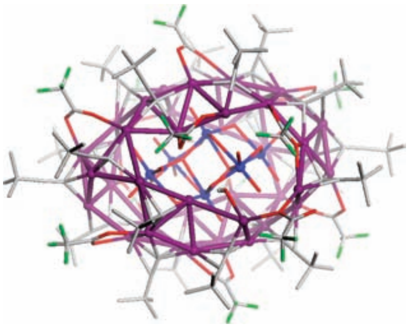

Figure 3. Perspective view of complex **2** (H atoms and bonds between Ag and O atoms of $[Mo_6O_{22}]^{8-}$ are omitted for clarity; color code: Mo, blue; O, red; Ag, dark violet; C, gray; F, green).

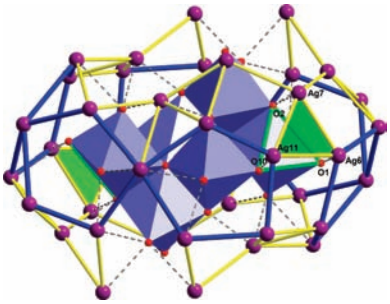

Figure 4. A combined view of complex **2** (all the organic ligands are omitted; $\{Ag_3O_3\}$ units and silver pentagons are highlighted; atom color code: O, red; Ag, dark violet).

The structural analyses of **1** and **2** demonstrate that the polyoxoanions with abundant surface oxygen atoms tend to induce the formation of the silver cluster shells via multiple Ag−O bonding interactions. In contrast, when the central polyoxoanion contains fewer surface O atoms, the silver(I) ions mainly arrange themselves to construct silver tetragons and pentagons. Thus the Ag−O coordination bonding and argentophilic Ag···Ag supramolecular interactions competitively coexist during the crystal growth of complexes **1** and **2**, yielding final structures that are largely determined by a balance of preponderant interactions. The results also indicate that the surface O atoms with higher charge densities better facilitate the formation of shell-type silver(I)−alkynyl clusters by Ag−O interactions. Thus globular polyoxoanions with more terminal O atoms may not be easily decorated by silver alkynyl groups.

The cluster complexes **1** and **2** are new fascinating nanomaterials in consideration of the following factors: (i) The cluster surface is populated by alkynyl or TFA ligands, which make these complexes soluble in organic solvents. (ii) The silver(I) ion is not only an excellent electron acceptor in chemical reactions but also sensitive to external optical stimulus. Such intrinsic nature enables silver(I)-abundant complexes to function as potentially useful catalysts or optical sensors. (iii) The encapsulated polyoxometalate may exhibit catalytic and photochemical activity, redox behavior. Therefore POM-based silver alkynyl materials offer promise of desirable physical or chemical properties due to the synergistic effect.

The solubility of **1** and **2** in methanol enabled us to investigate their nanoscale morphologies directly without additional treatment of surfactant. TEM images indicate that both samples exist as monodisperse particles (Figure S4). The averaged size of the identified particles is 2.6 and 2.5 nm, respectively, which are close to the maximum C···C separations in the clusters (2.38 nm for **1** and 2.32 nm for **2**) obtained from X-ray analyses. The TEM results affirm that acid-promoted facile synthesis is a viable route to generate POM-based silver alkynyl nanodot materials.

Cyclic voltammograms of **1** and **2** exhibit irreversible redox couples E_c/E_a (E_c, cathodic peak potential; E_a, anionic peak potential) of 355 mV/814 mV and 371 mV/723 mV, respectively (Figure S6). These peaks are very different from those observed for the $(Et_4N)_3[H_3V_{10}O_{28}]$ and $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ precursors but analogous to the redox couples of $AgNO_3$ in solution (E_c/E_a of 453 mV/611 mV). Thus, the redox peaks for **1** and **2** are attributed to Ag^0/Ag^+ couples arising from the peripheral silver(I) clusters, and the different E_c and E_a values suggest that the central polyoxoanions play a significant role in affecting the redox behavior. Controlled-potential electrolyses of the two complexes indicate a consumption of 24 and 26 electrons per molecule for **1** and **2**, respectively. Such multielectron transfer processes are first observed among the known multinuclear silver(I)−alkynyl compounds. This result also holds promise for the generation of mixed-valent silver(0,I) nanomaterials by electroreduction of preformed silver alkynyl clusters.

In summary, neutral POM-based silver alkynyl cluster complexes **1** and **2** have been synthesized using a facile acid-induced approach. In each case the central polyoxoanion is surface-modified by incorporation within a globular 40-vertex silver(I) alkynyl cluster. Specific ion-pair recognition between the polyoxometalate and silver(I) alkynyl supramolecular synthon has been observed, which leads to a better understanding of the reaction pathway and new insight to the rational design of multifunctional Ag(I)−POM complexes. Moreover, the new complexes are easily manipulated nanodot materials, the size of which can be controlled by modulating the central polyoxoanions.

Acknowledgment. This work is dedicated to the memory of Prof. Charles A. McDowell (1918−2001). We gratefully acknowledge financial support by the Hong Kong Research Grants Council (GRF ref. CUHK 402408), the Wei Lun Foundation, and a Research Fellowship (to G.-G.G.) from The Chinese University of Hong Kong.

Note Added after ASAP Publication. A duplicate reference was deleted in the version published ASAP December 4, 2009.

Supporting Information Available: Experimental details, X-ray crystallographic data in CIF format, syntheses and structural description of complexes **3** and **4**, and additional figures for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) **Syntheses. 1**: $AgC{\equiv}C^tBu$ (0.073 g, 0.386 mmol) was dissolved in methanol (5 mL) under stirring. Then 0.2 mL of CF_3COOH and $(Et_4N)_3[H_3V_{10}O_{28}]$ (0.012 g, 0.009 mmol) was added under stirring to form an orange suspension with pH *ca.* 3.5. After 12 h, an orange-red solution was collected by filtration. Slow evaporation afforded the product as orange-red crystals. Yield: *ca.* 24% (based on V). Elemental analysis (%) calcd for $Ag_{40}C_{160}F_{36}H_{214}O_{56}V_{10}$: Ag, 50.52; V, 5.96; C, 22.50; H, 2.53. Found: Ag, 50.67; V, 5.79; C, 22.62; H, 2.59. IR (KBr): 2005 ($C{\equiv}C$), 959, 916, 835, 800, 720 cm^{-1} ($[V_{10}O_{28}]^{6-}$). ^1H NMR ($CDCl_3$) δ 1.406 (s, $C(CH_3)_3$), 3.494 (s, $HOCH_3$). **2**: The procedure used for **1** was repeated with $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ (0.010 g, 0.007 mmol) as the polyoxometalate reactant. Colorless block-like crystals of **2** were deposited. Yield: *ca.* 22% (based on Mo). Elemental analysis (%) calcd for $Ag_{40}C_{146}F_{36}H_{188}Mo_6O_{48}$: Ag, 52.08; Mo, 6.95; C, 21.17; H, 2.29. Found: Ag, 51.91; Mo, 6.83; C, 21.35; H, 2.34. IR (KBr): 2008 ($C{\equiv}C$), 839, 800, 722, 614 cm^{-1} ($[Mo_6O_{22}]^{8-}$). ^1H NMR ($CDCl_3$) δ 1.382 (s, $C(CH_3)_3$), 3.496 (s, $HOCH_3$).

(16) **Crystallographic data. 1**: Monoclinic, $a = 18.9665(6)$ Å, $b = 22.4906(8)$ Å, $c = 32.4187(10)$ Å, $\beta = 109.313(2)°$, $V = 13050.6(7)$ Å^3, $T = 290$ K, space group $P2_1/c$, $Z = 2$, 197 033 reflections measured, 25 526 unique ($R_{int} = 0.0856$) which were used in all calculations. $R_1 = 0.0579$, $wR_2 = 0.1525$ for $I > 2\sigma(I)$. **2**: Monoclinic, $a = 22.290(3)$ Å, $b = 20.470(3)$ Å, $c = 27.561(4)$ Å, $\beta = 93.970(5)°$, $V = 12545(3)$ Å^3, $T = 290$ K, space group $P2_1/n$, $Z = 2$, 115 952 reflections measured, 24 459 unique ($R_{int} = 0.0485$) which were used in all calculations. $R_1 = 0.0583$, $wR_2 = 0.1536$ for $I > 2\sigma(I)$. CCDC 745356 for **1** and 745357 for **2**.

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JA907900B