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Acid–Base-Triggered Structural Transformation of a Polyoxometalate Core Inside a Dodecahedrane-like Silver Thiolate Shell

Hong Liu, Chao-Yu Song, Ren-Wu Huang, Yu Zhang, Hong Xu, Mei-Jia Li, Shuang-Quan Zang, and Guang-Gang Gao**

Dedicated to Professor Thomas C. W. Mak on the occasion of his 80th birthday

Abstract: *Self-assembly of metavanadate and organosilver(I) salts leads to a novel dodecahedrane-like* $[Ag_{30}(^tBuS)_{20}]^{10+}$ *silver(I) thiolate nanocage that tightly wraps an unusual* C_{2h} *polyoxovanadate anion. The polyoxovanadate core undergoes transformation to a* D_{3d} *configuration upon acidification, and reverts back to its original* C_{2h} *structure upon addition of base. Chromism was observed for the silver(I) thiolate cluster during the configurational change of the central polyoxovanadate core; the color of the solution changes reversibly from green to dark yellow. This work represents the first reported example of chromic polyoxometalate-templated silver(I) thiolate shells that respond to external acid–base stimuli. It also represents an important advance in providing crystallographic proof that structural transformations occur in a nanoscale core–shell cluster.*

A general and effective approach for the synthesis of organosilver(I) clusters[1–5] makes use of suitably selected template anions.[6,7] In particular, polyoxometalates (POMs)[8–10] have been amply demonstrated as versatile templates in the assembly of high-nuclearity silver(I) ethynide and thiolate cluster systems that manifest intriguing structures with potential applications as luminescent, sensory, and catalytic materials.[11–14] In most reported clusters, the silver(I) organic shells are usually built of multiple polygons with irregular shapes. Noting that silver(I) pentagon and hexagon have been sporadically observed in some irregular clusters,[15] we speculated that high-symmetry silver(I) alkynyl and thiolate cages may be accessible by utilizing judiciously chosen polyoxometalate templates.

The phenomenon of crystal transformation has attracted considerable attention and is usually observed in metal–organic coordination polymers,[16–19] however, monitoring structural transformation in nanoscale clusters by using single-crystal X-ray crystallography remains a difficult task. To the best of our knowledge, only one example of structural transformation between two isomers in thiolated metal nanoparticles has been reported to date.[20] As such, the structurally determined transformation of nanoclusters will not only extend the understanding of nanotechnology to the atomic level, but also may be helpful for identifying new smart nanosized functional materials that can undergo isomeric transformations. However, the observation of a structural transformation for core–shell thiolated metal nanoparticles by using single-crystal X-ray crystallography has yet to be reported.

Polyoxometalate anions can be easily transformed to other species by acidification in solution, and the new species may posess new chemical or physical properties.[21] However, the transformation of a polyoxometalate core in silver(I) alkynyl or thiolate nanosized cage clusters has not been reported to date. By restriction inside a nanosized cage, the transformation of the polyoxometalate core may modulate the properties of the external silver(I) alkynyl or thiolate shell, and possibly lead to new POM/organosilver(I) functional materials.

Herein we report how the self-assembly of metavanadate and silver(I) salts gives a novel cluster compound $[Ag_{30}(^tBuS)_{20}V^{V}_{10}V^{IV}_{2}O_{34}]\cdot 10\,CH_3OH$ (**1**; green), which contains an unprecedented silver(I) thiolate $Ag_{30}S_{20}$ dodecahedrane-like cluster shell wrapped around a $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ polyoxovanadate core. Subsequent addition of trifluoroacetic acid to a methanolic solution of **1** generates another derivative complex $[Ag_{30}(^tBuS)_{20}V^{V}_{10}V^{IV}_{2}O_{34}]\cdot 7CH_3OH$ (**2**; dark yellow) with its cluster shell intact, but the $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ core undergoes transformation to a higher-symmetry configuration. Furthermore, addition of triethylamine to a solution of **2** leads to $[Ag_{30}(^tBuS)_{20}V^{V}_{10}V^{IV}_{2}O_{34}]\cdot 8CH_3OH$ (**1a**; green) with its cluster shell and polyoxovanadate core virtually identical to that in **1**. To the best of our knowledge, this is the first report of such an acid–base triggered structural transformation of a polyoxometalate core inside a nanoscale cluster shell for high-nuclearity silver clusters.

Complex **1** was synthesized by the self-assembly of ammonium metavanadate, Ag^{t}BuS, and $AgBF_4$ in methanol/water (12:1 v/v mixture) at a starting pH value of 4.0. After heating in a Teflon autoclave at 65 °C for 48 h, complex **1** crystallized as green blocklike crystals at pH 6.0. Single-crystal X-ray analysis showed that **1** (space group *C*2/*m*) is a cationic cluster consisting of 30 silver(I) ions stabilized by

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[*] R.-W. Huang, Prof. Dr. H. Xu, Prof. Dr. S.-Q. Zang
College of Chemistry and Molecular Engineering
Zhengzhou University
Zhengzhou 450001 (China)
E-mail: zangsqzg@zzu.edu.cn

Dr. H. Liu, C.-Y. Song, Y. Zhang, M.-J. Li, Prof. Dr. G.-G. Gao
Department of Chemistry, College of Pharmacy
Jiamusi University, Jiamusi 154004 (China)
E-mail: gaogg@jmsu.edu.cn

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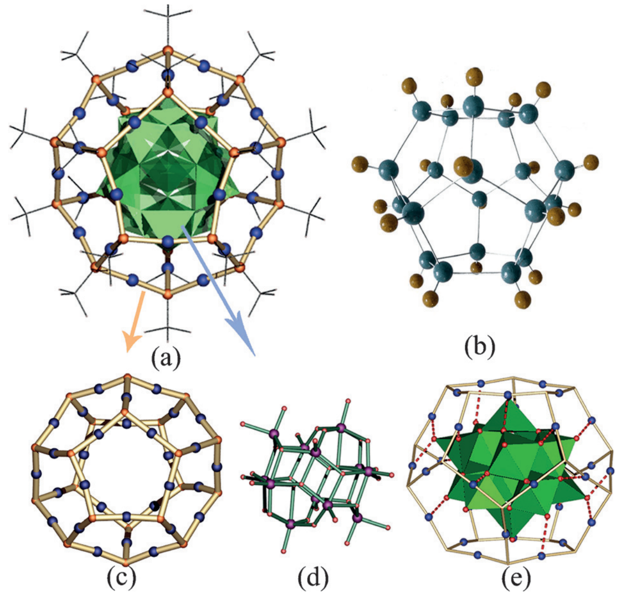

Figure 1. a) Perspective view of host–guest cluster assembly in **1**. b) Ball-and-stick model of dodecahedrane (C blue green; H brown). c) $Ag_{30}S_{20}$ cage in **1** viewed along its idealized S_{10} axis (*tert*-butyl groups and $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ core are omitted for clarity). d) Ball-and-stick representation of $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ core. e) Lateral view of linkage of $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ core to facial Ag^{I} atoms of a $Ag_{30}S_{20}$ cage (*tert*-butyl groups are omitted for clarity). Color code: Ag blue; V purple; S orange; O red; C gray.

centripetal *tert*-butyl mercaptan groups and a $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ polyoxoanion at its center (Figure 1 a). Each $^{t}BuS^{-}$ ligand adopts the μ_3-η^1, η^1, η^1 ligation mode to link three silver ions with Ag–S distances in the range of 2.318(5)–2.400(5) Å. Each silver(I) ion links two neighboring S^{2-} ions to form an almost linear S-Ag-S subunit with angles in the range of 167.75(16)–177.9(2)°. Five S-Ag-S subunits share S^{2-} vertices to form an almost regular pentagon, and twelve pentagons come together to constitute a 5^{12} dodecahedral topological cage (Figure 1 c). The S–S distances are in the range of 4.632(12) to 4.758(10) Å, which indicate a slight deviation from the regular dodecahedron. Notably, this is the first reported silver(I)–organic dodecahedral nanosized cluster, which is analogous to dodecahedrane (Figure 1 b). In fact, pentagons and hexagons, which are basic building units in fullerene-like compounds, are both also geometrically important polygons in Platonic solids.[22] However, the artificial nanoscale molecular polygons are not easily obtained because of the difficulty of atomic-level modulation when using limited macroscopic synthetic methods.[23]

The central $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ polyoxoanion of C_{2h} symmetry comprises six VO_6 octahedra in two groups, four VO_5 square-pyramids in two groups, and two capping VO_4 tetrahedra (Figure 1 d). Ten vanadium atoms are in the +5 state and two vanadium atoms are in the +4 state, as confirmed by XPS analysis (Figure S4). Such polyoxovanadate compounds differ slightly from known $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ polyoxovanadate cluster,[24] in which the capping units are distorted $VO_4F(H_2O)$ octahedra. The surface oxygen atoms can be classified as terminal, μ_2, and μ_3 bridging types and show different orientations to the outer silver(I) thiolate shell. Ten of the terminal oxygen atoms are each located almost at the center of a pentagon, while two oxygen atoms from the VO_4 tetrahedra deviate from the pentagonal center. Eight terminal and ten bridging oxygen atoms coordinate to neighboring silver(I) centers at Ag–O distances in the range of 2.45(2) to 2.51(3) Å to fix the central polyoxovanadate core within the silver thiolate shell (Figure 1 e). As shown in Figure S6(A), each dodecahedron in **1** is surrounded by twelve neighboring dodecahedra. Along the *c* axis, adjacent pentagons belonging to different dodecahedral cages bear a face-to-face relationship at a centroid-to-centroid separation of 8.21 Å. Along other directions, neighboring cage pentagons are arranged in an offset fashion with centroid-to-centroid distances in the range of 9.28–10.46 Å.

Most interestingly, addition of trifluoroacetic acid to a methanolic solution of **1** generates derivative cluster complex **2** (space group $R\bar{3}m$), in which the central polyoxovanadate anion transforms into a new $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ species of higher D_{3d} symmetry, whilst its silver thiolate shell remains virtually unchanged (Figure 2 top left). The XPS results show that two vanadium atoms are in the +4 state for

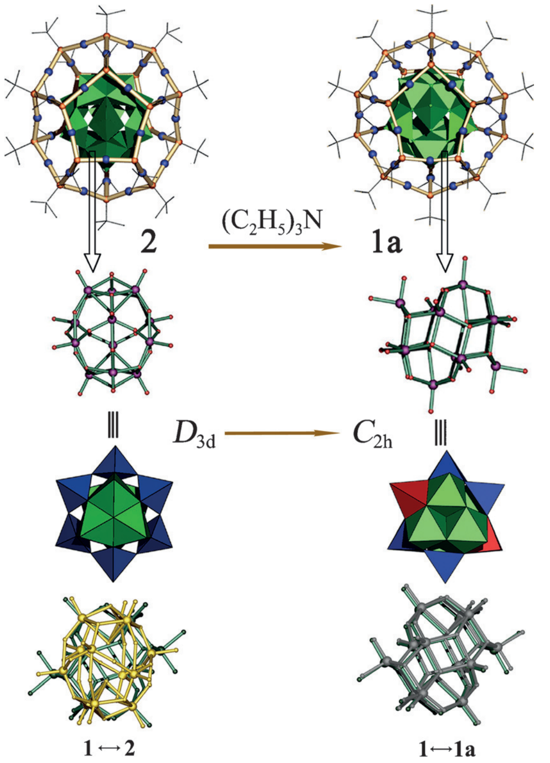

Figure 2. First row compares the $[Ag_{30}(^{t}BuS)_{20}]^{10+}$ shells (ball-and-stick models) wrapping tightly around their $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ cores (polyhedral models) of the host-guest cluster assemblies in **2** and **1 a** viewed down their respective idealized S_{10} symmetry axes. The second and third rows compare the two polyoxovanadate cores viewed laterally (ball-and-stick) and in projection (polyhedral). In the last row, the left-hand side shows an overlap of the $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ core in **1** (dark green) and $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ core **2** (yellow); the right-hand side shows a slightly offset overlap of the $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ core in **1** (dark green) and $[V^{V}_{10}V^{IV}_{2}O_{34}]^{10-}$ core **1 a** (gray). Color code for ball-and-stick models: Ag blue; V purple; S orange; O red; C gray.

all complexes, thus indicating that the reduced vanadium atoms are stable in the silver(I) thiolate cage (Figure S4). This is also the first report of the observation of reduced polyoxometalate in a nanosized cage. In contrast to the C_{2h} central core in **1**, the $[V^{V}{}_{10}V^{IV}{}_{2}O_{34}]^{10-}$ polyoxoanion in **2** (Figure 2, second row, left) comprises six VO_6 octahedra and six VO_5 square pyramids. The surface oxygen atoms can be classified as terminal, μ_2, and μ_3 bridging types, which show different orientations with respect to the outer silver(I) thiolate shell. Twelve terminal O atoms are each located around the center of a pentagon. Some of the terminal and bridging oxygen atoms coordinate to neighboring silver(I) centers at Ag–O distances in the range of 2.480(30) Å to 2.691(20) Å to fix the central polyoxovanadate core within the silver thiolate shell.

Moreover, the introduction of an organic base into a solution of **2** generates complex **1a** (Figure 2, top right) that is almost isostructural to **1**. The overlapped figures for these polyoxoanionic cores illustrate their configurational transformation for complexes **1**, **2**, and **1a** (Figure 2, bottom). As a result, complex **1** can be considered as a smart system, with its central polyoxovanadate core possessing the ability to transform into a higher- or lower-symmetry configuration in response to acid–base stimuli. It should be noted here that such a stimuli-response phenomenon may provide new insights into the origin of life in terms of the behavior of inorganic compounds in a confined cluster. In addition, acid–base stimuli also induces change in stacking of the host–guest complexes.

Complexes **1**, **1a**, and **2** are soluble in most organic solvents but are insoluble in water. In a methanolic solution, TEM images indicate that all these samples exist as nanosized particles (Figure S7), of which the average particle size (2.5 for **1**, 2.6 for **2**, and 2.6 for **1a**) is only slightly larger than the values determined by the longest carbon-to-carbon distances in the clusters as 1.87 nm for **1**, 1.87 nm for **2**, and 1.88 nm for **1a**. This result suggests that the clusters of these complexes are stable and maintain their nanosized structures. Furthermore, complex **1** exhibits interesting acid–base chromatic properties. As shown in Figure 3, upon addition of trifluoroacetic acid (30 µL) to a methanolic solution of **1**, the color changes from green to dark yellow. After further addition of triethylamine (30 µL), the solution regains its green color. Based on the structural analysis results, this phenomenon is related to the reversible interconversion of distinct polyoxovanadate core configurations. Such a property shows **1** to be a new kind of chromatic material that readily responds to external acid–base stimuli.

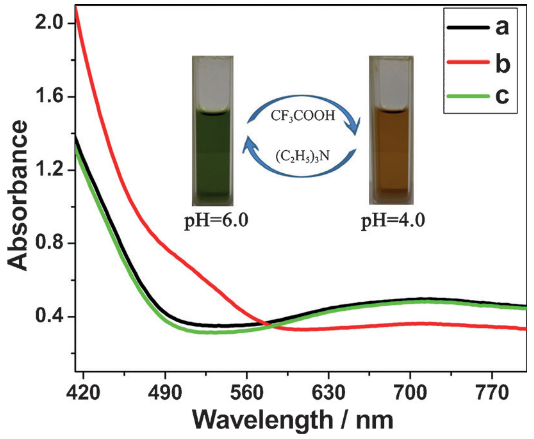

Figure 3. UV/Vis spectra of complex **1** (0.4 mmol L^{-1}) in methanol (a), after addition of 30 µL trifluoroacetic acid (b), and further addition of 30 µL triethylamine (c).

In summary, a newly synthesized POM-based 20-vertex globular organosilver(I) core–shell cluster **1** has been shown to feature a novel dodecahedral silver thiolate cage that accommodates an unusual polyoxovanadate central core. The POM core in **1** can undergo acid–base induced transformation; this is the first report of this phenomenon among known core–shell silver(I)-thiolate clusters and opens a new avenue to artificial intelligent core–shell clusters based on inorganic–organic complex assembly. This work not only confirms that structural transformations of core–shell silver(I)-thiolate cluster can be monitored by X-ray crystallography, but also provides access to the controllable synthesis of core–shell clusters at the atomic level.

Experimental Section

Synthesis of $[Ag_{30}({}^{t}BuS)_{20}V^{V}{}_{10}V^{IV}{}_{2}O_{34}]\cdot 10CH_3OH$ (**1**): $AgS^{t}Bu$ (0.0394 g, 0.239 mmol) was dissolved in methanol (6 mL) under stirring. $AgBF_4$ (0.0205 g, 0.105 mmol) was added with sonication for 30 min,and then a NH_4VO_3 solution (0.0241 g, 0.206 mmol NH_4VO_3, 300 µL H_2O) was added to the mixture after several minutes. The resulting yellow suspension was sealed and heated at 65 °C for 48 h. After cooling to room temperature, the resulting green solution was filtered and the filtrate left to evaporate slowly in the dark for 6 weeks. Green crystals of **1** were collected and washed with a small quantity of water and Et_2O (yield 17.0 mg, 21.6 %, calculated from Ag). Elemental analysis (%) calcd for $C_{90}H_{220}Ag_{30}O_{44}S_{20}V_{12}$: C 16.64, H 3.41, found: C 16.61, H 3.37; FTIR (KBr): $\tilde{\nu}$ =936, 833, 758, 724, 574 cm^{-1} (for $[V_{12}O_{34}]^{10-}$). CCDC 1048154 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of $[Ag_{30}({}^{t}BuS)_{20}V^{V}{}_{10}V^{IV}{}_{2}O_{34}]\cdot 7CH_3OH$ (**2**): Compound **1** (0.2500 g) was dissolved in methanol (5 mL), and then trifluoroacetic acid (2 mL) was added and the color of the solution changed from green to yellow. After stirring for 2 h, the solution was filtered, and the filtrate was left to evaporate slowly in the dark to result in dark yellow crystals of **2** after 3 weeks (yield 39.5 mg, 15.8 %, calculated from Ag). Elemental analysis (%) calcd for $C_{87}H_{208}O_{41}S_{20}Ag_{30}V_{12}$: C 16.33, H 3.28, found: C 16.28, H 3.22; FTIR (KBr): $\tilde{\nu}$ =943, 836, 795, 758, 724, 575 cm^{-1} (for $[V_{12}O_{34}]^{10-}$). CCDC 1063407 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

$[Ag_{30}({}^{t}BuS)_{20}V^{V}{}_{10}V^{IV}{}_{2}O_{34}]\cdot 8CH_3OH$ (**1a**): 0.1500 g of **2** was dissolved in 5 mL methanol, and then 0.5 mL triethylamine was added to obtain a green solution. After stirring for 2 h, the solution was filtered and the filtrate left to evaporate slowly; green crystals of **1a** were deposited after 3 weeks in the dark (yield 37.5 mg, 25.0 %, calculated from Ag). Elemental analysis (%) calcd for $C_{88}H_{212}O_{42}S_{20}Ag_{30}V_{12}$: C 16.44, H 3.32, found: C 16.47, H 3.27; FTIR (KBr): $\tilde{\nu}$ =932, 830, 757, 723, 575 cm^{-1} (for $[V_{12}O_{34}]^{10-}$). CCDC 1063408 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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